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Transition Metal Catalyzed C-C Bond Formation via Transfer Hydrogenation; From Methodology Development to Polycyclic Aromatic Hydrocarbon Syntheses

Committee:

Michael J. Krische, Supervisor

Eric V. Anslyn

Jonathan L. Sessler

Hung-Wen (Ben) Liu

Sean T. Roberts

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Hiroki Sato

Dissertation

Presented to the Faculty of the Graduate School of

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Dedication

To my family

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Abstract

Transition Metal Catalyzed C-C Bond Formation via Transfer Hydrogenation; From Methodology Development to Polycyclic Aromatic Hydrocarbon Syntheses

Hiroki Sato, Ph.D.

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Supervisor: Michael J. Krische

Since the Nobel prize-winning discovery of the Diels-Alder reaction in 1928, cycloaddition reactions—chemical transformations to construct ubiquitous cyclic organic molecules—are one of the most important chemical reactions found in physical, biological, and organic chemistry. Despite their long history, cycloaddition reactions only proceed with a limited combination of π-unsaturated compounds, imposing severe limitations on their scope and applications in organic synthesis. By exploiting transition metal catalyzed transfer hydrognenation reactions and C-C formation, I disclosed a series of novel cycloaddition reactions starting from diols, an abundant and inexpensive compounds easily obtained from biomass. Because of the expediency with which diols can be accessed or their status as feedstock materials, these reactions represent a paradigmatic shift in the synthetic efficiency of cycloaddition reactions for building complex ring systems.

Furthermore, those new methodologies were applied to a different and emerging field for our group: material science. Polycyclic aromatic hydrocarbons (PAHs) consist of conjugated aromatic rings and have attracted the attention of material scientists for their excellent electronic properties. Presently, over 3 million PAHs have been reported and synthesized. As the structural complexity of PAHs has greatly increased over the past two decades, the methodologies capable of accessing PAHs has remained stagnant following the introduction of the cross coupling reaction. By taking advantage of the newly developed cycloaddition methodologies, PAHs that are synthetically difficult or impossible with conventional methodologies could be realized. Our new cycloaddition methodology followed by simple dehydration yields PAHs using inexpensive and chemically stable diols. Moreover, our new methodology is highly functional group tolerant, including towards halides, allowing complimentary cross coupling methods to further functionalize the products. The hybridization of old and new technologies could derivatize well-known PAHs to novel structures with unusual symmetry and highly conjugated π-system. Consequently, I achieved the syntheses of hexabenzocoronene (HBC) with a new symmetry, S-doped helicene including picene moiety, and novel all-aromatic helical cages. Therefore, new methodologies for PAH construction that compliment current strategies will dramatically extend the types of materials that can be synthesized, including challenges unmet in material science.

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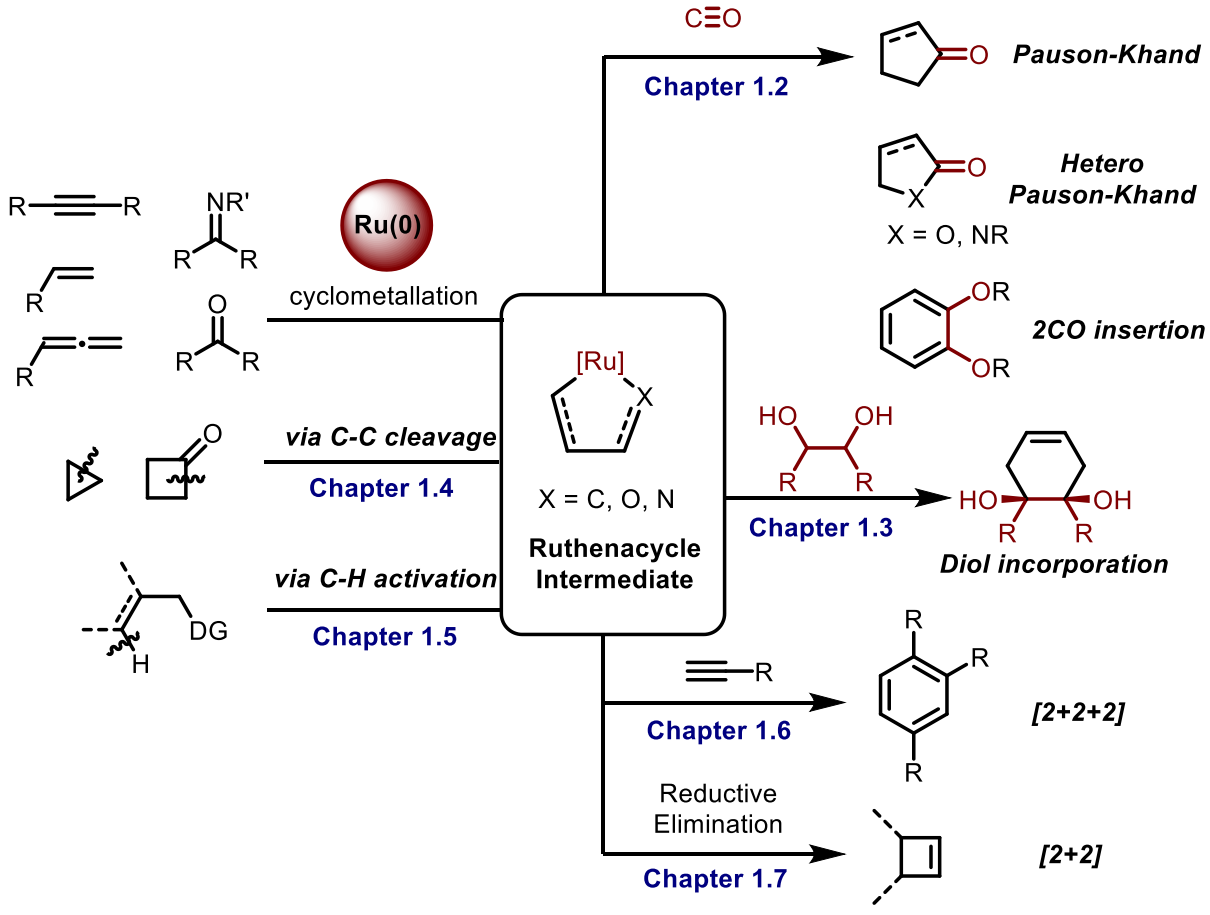
Chapter 1: Ruthenium (0) Catalyzed Cycloaddition Reactions

1.1 Introduction

Cycloaddition reactions, which allow multiple components to be assembled intermolecularly to form synthetically and biologically important ring systems, are one of the most efficient ring-forming methodologies in organic synthesis. Historically, the discovery of photocycloaddition[1] in 1908 and the Diels-Alder reaction[2] in 1928 has led to many distinct and powerful cycloaddition reactions. Later, emerging transition metal catalysis has dramatically expanded the scope of the cycloaddition chemistry until today.[3] Zerovalent ruthenium catalyzed cycloaddition reactions (Scheme 1.1) have generated much attention for their unique reactivities fundamentally different from higher valent ruthenium catalysis[4] by readily incorporating carbon monoxide or a carbonyl group into the cycloadduct products. While several Ru(0) catalyzed [2+2+2] and [2+2] cycloadditions were reported as analogies of cobalt catalyzed reactions, the first report of carbon monoxide insertion and cycloaddition with a $Ru_3(CO)_{12}$ catalyst by the Murai group[5] in 1993 shed light on this distinctive Ru(0) chemistry. Subsequently, these intriguing Ru(0) abilities lead to the pioneering work of catalytic Pauson-Khand reactions (Chapter 1.2.1), developed by Murai[6] and Mitsudo[7] independently in 1997. Application of these carbonylative reactions to unsaturated compounds including heteroatoms resulted in the development of hetero-Pauson-Khand reactions as useful synthetic methods for lactones and lactams (Chapter 1.2.2, 1.2.3) by Murai, Imhof, and Takahashi groups. Later in 2013, the Krische group found that a Ru(0) catalyst was able to assemble 1,2-diols as a C2 building block in the cycloaddition reaction to form novel highly substituted 1,2-diol cycloadducts (Chapter 1.3). On the other hand, in 1994 Mitsudo group found that the Ru(0) was able to cleave C-C bonds at mild conditions and is capable of catalytic process.[8] This intriguing reactivity expanded the pathways and starting substrates to

generate ruthenacycle intermediates, which resulted in other novel cycloaddition reactions merging with carbonylative reactions (Chapter 1.4). Emerging C-H activation[9] also allowed unconventional substrates to form ruthenacycles via inactive C-H bonds cleavage (Chapter 1.5).

The materials covered in this chapter will be cycloaddition reactions with Ru(0) catalyst. Cyclization reactions, which form the rings intramolecularly, or annulation reactions to construct rings in multiple-steps via cyclization will not be covered. Cycloaddition reactions with stoichiometric amount of ruthenium metal are not described. In the later chapters, I demonstrate our new ruthenium(0) catalyzed cycloaddition reactions with diols and their applications to polycyclic aromatic hydrocarbons syntheses.



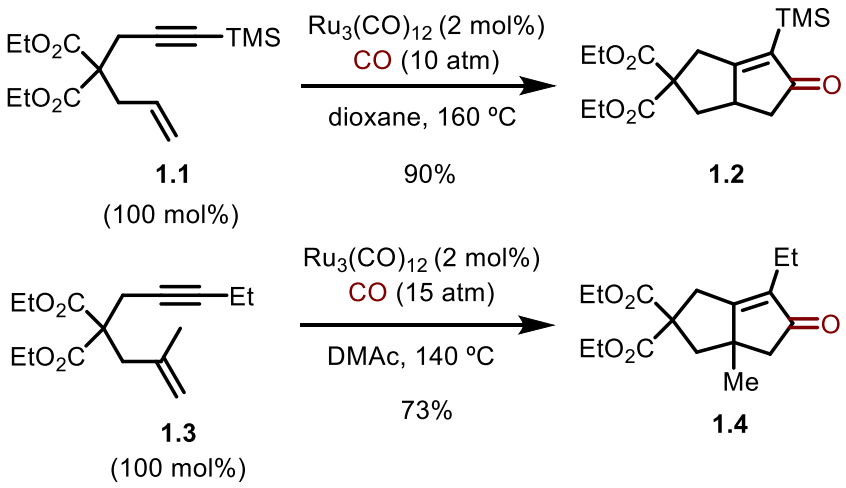
Scheme 1.1 Ru(0) catalyzed cycloaddition reactions.

1.2 Carbon monoxide incorperated cycloadditions

1.2.1 Pauson-Khand reaction

Pauson-Khand reactions,[10] which employ carbon monoxide, alkene, and alkyne are one of the most powerful methods to construct biologically important cyclopentenone moieties. While stoichiometric Pauson-Khand reactions had been well known with Co, Cr and W, few catalytic reactions were reported at the early stage.[11] The pioneering work of catalytic Pauson-Khand reactions with ruthenium catalysts were reported by the Murai[6] and Mitsudo[7] groups independently in 1997 (Scheme 1.2). The reaction of 1,6-enyne (**1.1**) with a catalytic amount of $Ru_3(CO)_{12}$ under 10 atm carbon monoxide pressure at 160 ˚C gave the corresponding bicyclo[3.3.0]octenone product (**1.2**) in good yield (Scheme 1.2 top). The scope of the alkene was limited to mono-substituted terminal alkenes as more substituted or 1,7- enynes didn't give the desired products.

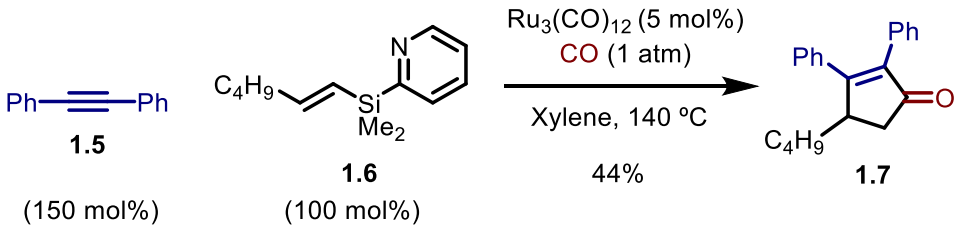
The Mitsudo group also reported the same reaction with pretty similar conditions (Scheme 1.2 bottom). Despite the small difference, their conditions with DMAc as solvent under 15 atm carbon monoxide pressure at 140 ˚C was able to efficiently progress with di-substituted alkenes.



Scheme 1.2 Ru(0) catalyzed Pauson-Khand reactions.

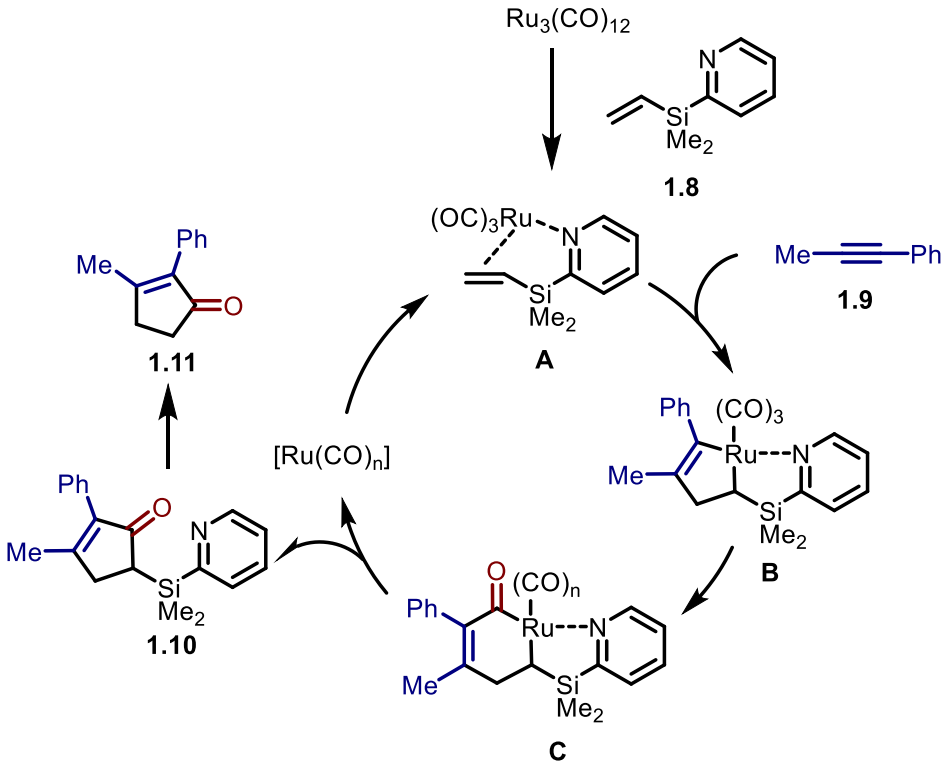
Interestingly, with Ru(cod)(cot) (cot = cycloocta-1,3,5-triene) catalyst was employed instead of of $Ru_3(CO)_{12}$ dealkoxycarbonylated cycloadducts were produced.

In 2002, the Yoshida group achieved the first intermolecular three component Pauson-Khand reaction with alkenes (Scheme 1.3).[12,13] Enhancement of the catalytic reactivity by the removable directing group dimethyl(2-pyridyl)silyl enabled convergent highly substituted cyclopentenones synthesis in complete regioselective manners. The treatment of diphenyl acetylene and the alkene (**1.6**) bearing the pyridyl directing group with a catalytic amount of $Ru_3(CO)_{12}$ under atmospheric carbon monoxide pressure resulted in the corresponding cyclopentenone derivative (**1.7**) in moderate yield. [1,3]-silyl migration followed by hydrolysis of the enolsilane might occur, which resulted in no silylated cyclopentenone observation after the cycloaddition reaction.



Scheme 1.3 3-components Pauson-Khand reaction with directing group.

Further mechanistic investigation was conducted by the group (Scheme 1.4).[14] The reaction was thought to begin with the coordination of ruthenium to the dimethyl(2-pyridyl)silyl directing group. Then, oxidative cyclometallation with alkyne generates ruthenacycle intermediate **B**. Successive migratory insertion of carbon monoxide ligand and reductive elimination release the ruthenium(0) and the silylated cycloadduct intermediate (**1.10**), which is readily desilylated to give the cyclopentenone (**1.11**). The isolation of ruthenium-dimethyl(2-pyridyl)silyl complex **A** and ruthenacycle intermediate **B** support this plausible mechanism.

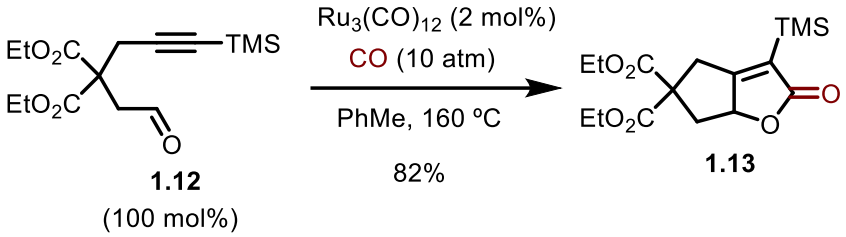


Scheme 1.4 Plausible mechanism of 3-components Pauson-Khand reaction.

1.2.2 Hetero Pauson-Khand reactions with aldehyde or ketone

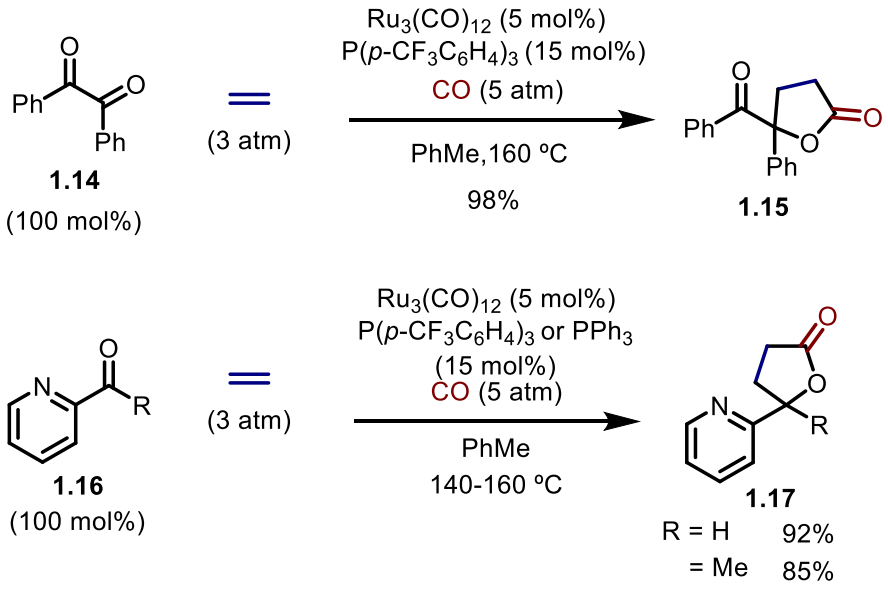
While 5-membered carbocycle syntheses were well known as the Pauson-Khand reaction, hetero Pauson-Khand reactions assembling heteroatom including unsaturated compounds and carbon monoxide are an efficient strategy to obtain lactone or lactam products. However, strong coordination of the heteroatom to the metal prevented the development of this type of reaction.[15] In 1998 the Murai group achieved the first example of hetero Pauson-Khand reactions exploiting $Ru_3(CO)_{12}$ catalyst and reaction conditions discovered in the previous year (Scheme 1.5).[16] The reaction of yne-aldehyde with a catalytic amount of $Ru_3(CO)_{12}$ and under carbon monoxide pressure at 160 ˚C provided α,β-unsaturated-γ-butyrolactones. No desired cycloadducts were

observed when other metal catalysts such as $Ru(CO)_2(PPh_3)_3$, $[RuCl_2(CO)_3]_2$, $Ru(acac)_3$, $Co_2(CO)_8$, $Rh_4(CO)_{12}$, $RhCl(PPh_3)_3$, or $Ir_4(CO)_{12}$ were employed.

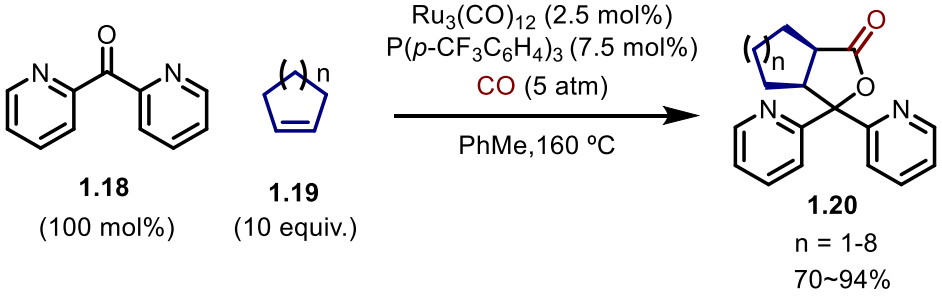


Scheme 1.5 Hetero Pauson-Khand reaction with yne-aldehyde.

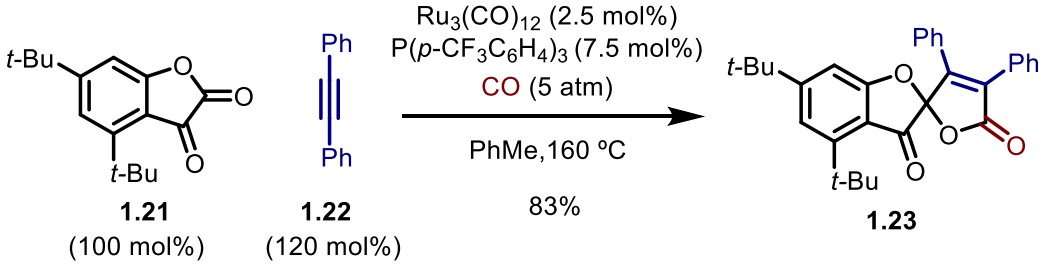
Murai also disclosed that this system was able to progress with ketones in place of aldehyde reactants (Schemes 1.6-1.8).[17] Treatment of a ketone with a catalytic amount of $Ru_3(CO)_{12}$ under ethylene and carbon monoxide pressure at high temperature resulted in the corresponding γ-butyrolactone (Scheme 1.6). This reaction worked with activated ketones such as α-keto esters, diones, heterocyclic substituted ketones. Interestingly, no cycloaddition reactions were observed with other metal carbonyls including $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$ or other ruthenium source such as $[RuCl_2(CO)_3]_2$, $RuCl_2(PPh_3)_3$, and $CpRuCl(PPh_3)_2$. Yields of these reactions with some substrates were improved with a triarylphosphine additive although the reason was not clear. Successively they dramatically expanded the scope of the unsaturated coupling partners instead of ethylene. Substituted alkenes, cyclic alkenes, and alkynes were also incorporated with aldehydes or ketones (Schemes 1.7, 1.8).[18,19]. Later in 2002, the Hong group reported the intramolecular reaction with allene-aldehydes to give α-methylene-γ-butyrolactones (Scheme 1.9).[20]



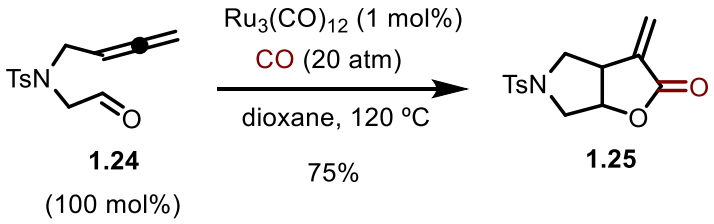
Scheme 1.6 Hetero Pauson-Khand reactions with ketone and ethylene.



Scheme 1.7 Hetero Pauson-Khand reaction with ketone and alkenes.

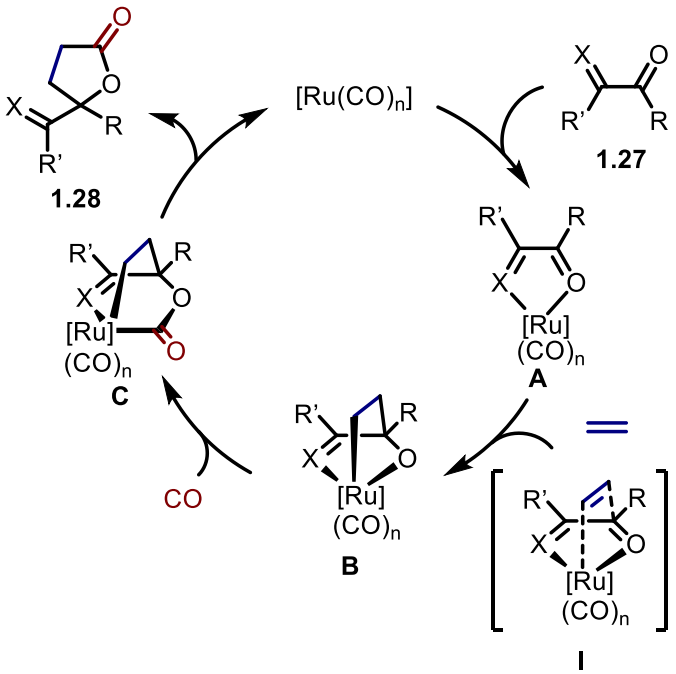


Scheme 1.8 Hetero Pauson-Khand reaction with ketone and alkyne.



Scheme 1.9 Hetero Pauson-Khand reaction with allene-aldehyde.

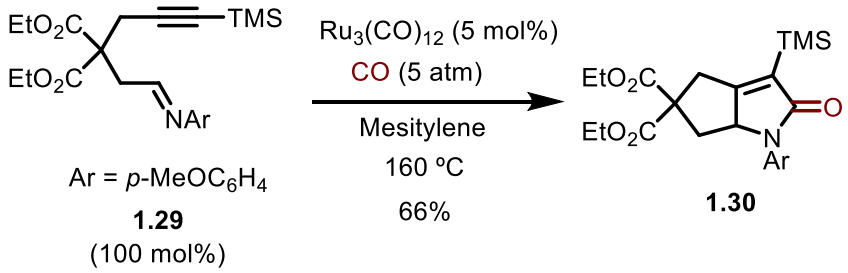
The proposed mechanism is shown in scheme 1.10. The first step of this transformation is the chelation of ruthenium to the activated bidentate ketone. Subsequent coordination of the alkene and an oxidative cyclometallation at the ruthenium center give the ruthenium complex **B**. The similar diaza-ruthenium carbonyl complex[21] and aza-oxo-iron carbonyl complex[22] were reported by other groups in stoichiometric reactions. Then, carbon monoxide insertion and reductive elimination furnished the final product lactone.



Scheme 1.10 Proposed mechanism of hetero Pauson-Khand reaction.

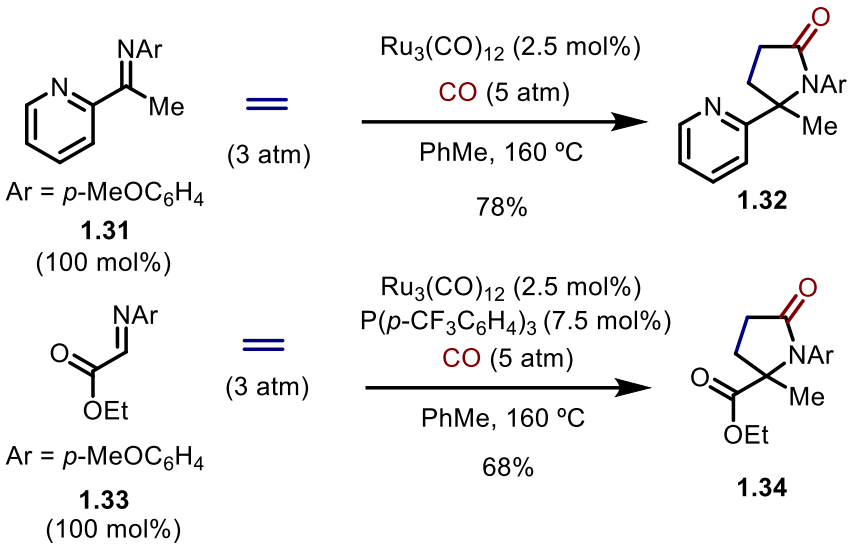
1.2.3 Hetero Pauson-Khand reactions with imines

During the course of the development of the hetero Pauson-Khand reactions, the Murai group found that imines instead of carbonyl compounds were also applicable to the catalytic reactions to form lactams. The reaction of 1,6-yne-imines with a catalytic amount of $Ru_3(CO)_{12}$ under carbon monoxide pressure at 160 ˚C in mesitylene gave the bicyclic α,β-unsaturated γ-lactams in moderate to good yield (Scheme 1.11).[23] Treatment of the 1,7-yne-imine also provided the corresponding δ-lactams. This reaction was ineffective with terminal alkynes, which only gave dihydropyridine derivatives without carbon monoxide insertion.

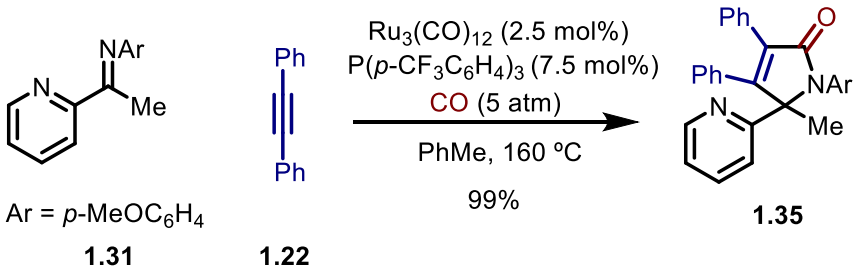


Scheme 1.11 Hetero Pauson-Khand reaction with yne-imine.

This reaction system was also applicable to intermolecular 3-components hetero Pauson-Khand reactions (Schemes 1.12, 1.13).[24] Under the same condition with or without a phosphine additive, reaction of heteroaromatic substituted ketimine or α-amino ester provided the corresponding γ-lactams. Substituted alkenes used in place of ethylene also afford γ-lactams as the diastereo mixtures. This reaction also proceeded with alkyne reactants instead of alkenes to produce unsaturated γ-lactams (Scheme 1.13).

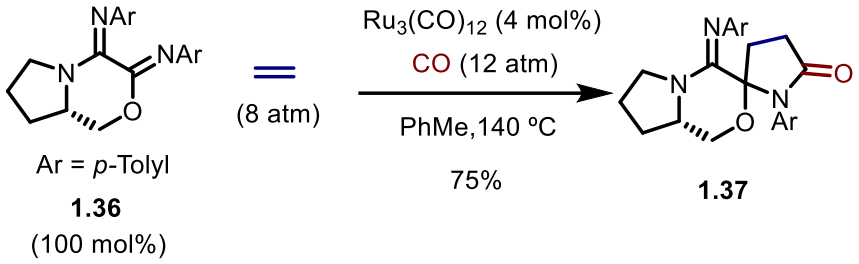


Scheme 1.12 3-Components hetero Pauson-Khand reactions with imine and ethylene.



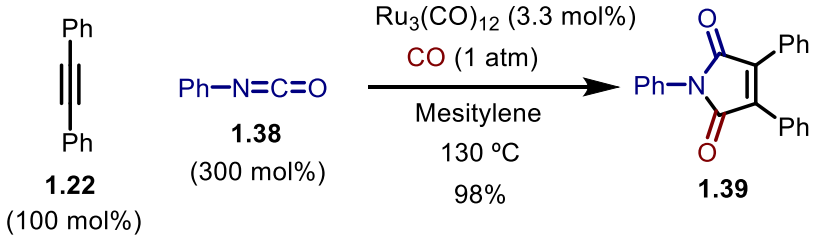
Scheme 1.13 3-Components hetero Pauson-Khand reactions with imine and alkyne.

While diimines were well known to chelate to ruthenium or iron carbonyls forming stable metal-diaza complexes, the catalytic hetero Pauson-Khand reaction had not been reported for a long time. In 2001, Imhof and coworkers demonstrated that a diimine was able to be incorporated in catalytic hetero Pauson-Khand reactions (Scheme 1.14).[25] The reaction of diimine **1.36** with $Ru_3(CO)_{12}$ under ethylene and carbon monoxide pressure at 140 ˚C furnish γ-lactams in a regioselective manner. Later, they also reported that mono-substituted alkene as well as ethylene was applicable to the reactions.[26]

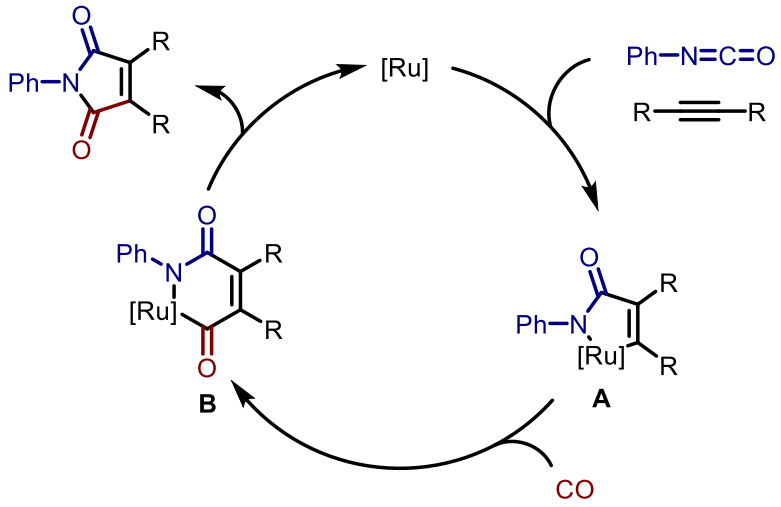


Scheme 1.14 Hetero Pauson-Khand reactions with diimine.

In addition to hetero Pauson-Khand reactions with carbonyl compounds or imines, this Ru(0) catalyst system is able to employ other novel coupling partners to provide alternate cycloadducts besides lactones or lactams. In 2006, the Kondo group reported the first catalytic intermolecular hetero Pauson-Khand reactions with isocyanate (Scheme 1.38).[27,28] With a $Ru_3(CO)_{12}$ catalyst, isocyanate and alkyne under carbon monoxide atmospheric pressure highly substituted maleimides were obtained in excellent yield. Other ruthenium sources $Ru(CO)_3(PPh_3)_2$, $RuH_2(CO)(PPh_3)_3$, and $RuHCl(CO)(PPh_3)_3$ showed much lower reactivity while $[RuCl_2(CO)_3]_2$, Cp*RuCl(cod), and CpRuCl(cod) completely shut down the reaction. The proposed mechanism was shown in scheme 1.16. The first step of the reaction is cyclometallation with one isocyanate and one alkyne to form the azaruthenacyclopentenone **A**. Successive migratory insertion of carbon monoxide and reductive elimination produce the maleimide.



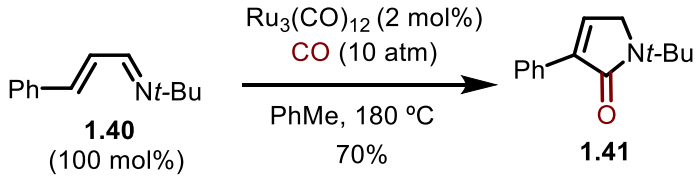
Scheme 1.15 Hetero Pauson-Khand reactions with isocyanate.



Scheme 1.16 The proposed mechanism of hetero Pauson-Khand reactions with isocyanate.

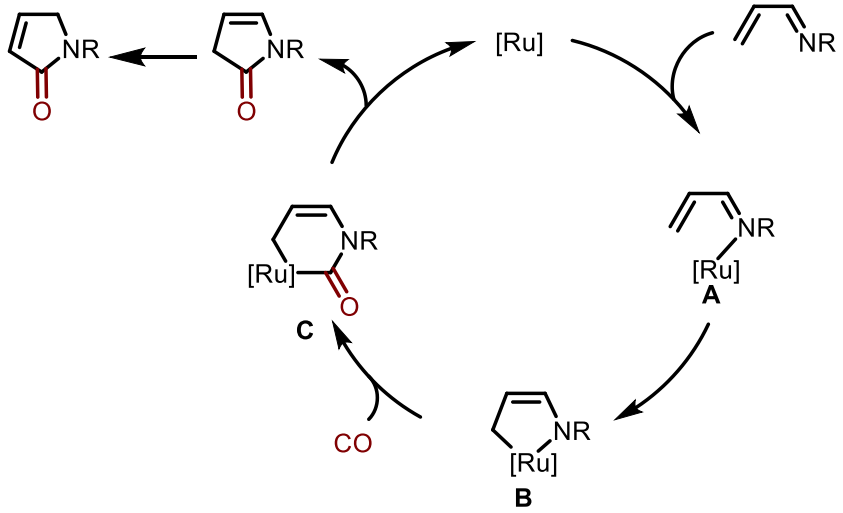
1.2.4 Other carbonylative cycloaddition reactions

In the course of the development of the catalytic hetero Pauson-Khand reactions, other unsaturated substrates were found to be used to construct heterocycles in different pathways. In 1999, Murai reported the ruthenium catalyzed [4+1] cycloaddition reactions between carbon monoxide and α,β-unsaturated imines (Scheme 1.17).[29] This reaction in the presence of carbon monoxide pressure and a catalytic amount of $Ru_3(CO)_{12}$ produced γ-lactams. The substituents on the amine was important. While a *t*-Bu group gave the desired cycloadducts, other substituents such as *i*-Pr, *n*-Bu, and *p*-$MeOC_6H_4$ failed to produce the desired produts. The possible mechanism is shown in scheme 1.18. Ruthenacycle **B** is formed coordinating to the imine. Successive migratory insertion of carbon monoxide into Ru-N bond leads to 6-membered ruthenium complex



Scheme 1.17 Carbonylative [4+1] cycloaddition reaction with α,β-unsaturated imine.

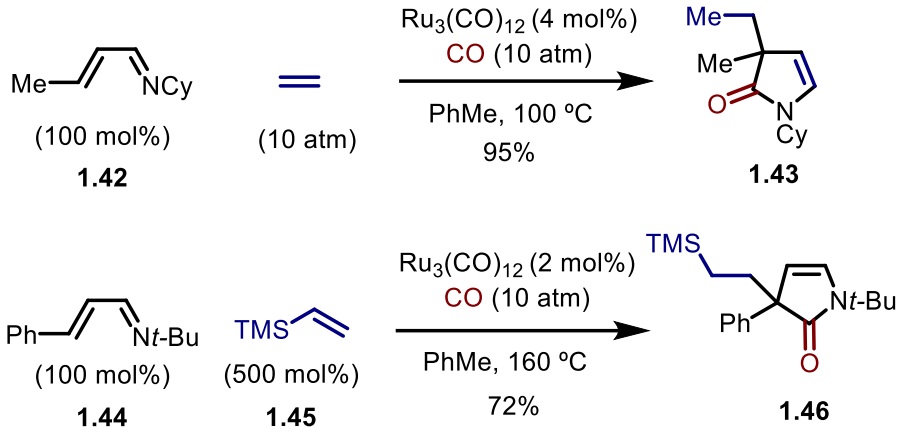
C. Next reductive elimination produces the enamine, which is isomerized to give the final products.



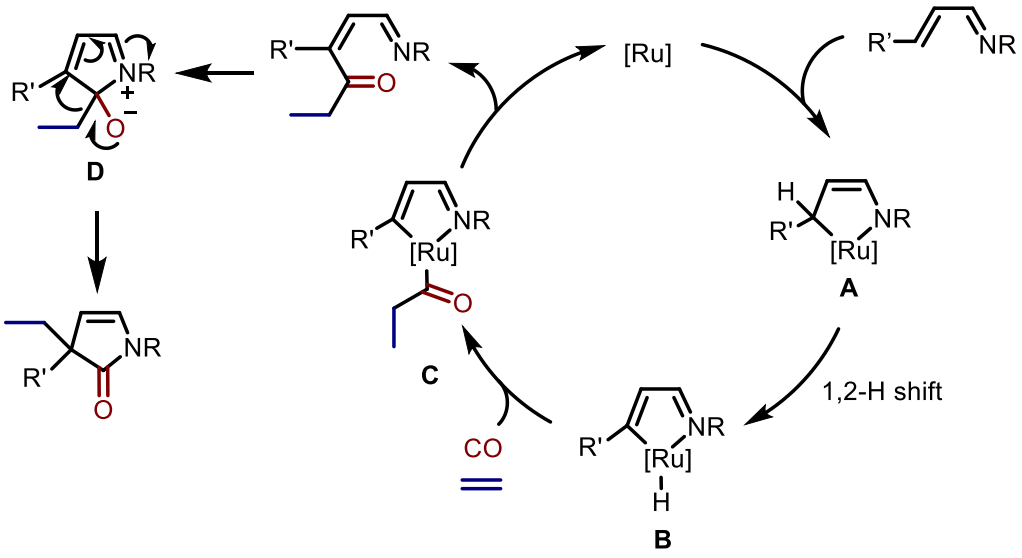
Scheme 1.18 Proposed mechanism of [4+1] cycloaddition with α,β-unsaturated imine.

In the same year, Imhof reported the three component reactions with ethylene gas (Scheme 1.19 top).[30] The reaction of an α,β-unsaturated imine under ethylene and carbon monoxide pressure with a $Ru_3(CO)_{12}$ catalyst lead to γ-lactam productswith one ethylene inserted. Substituent groups on the nitrogen atom were crucial. With *p*-$CF_3C_6H_4$ or Ph groups, the mixture of the cycloadducts and linear byproducts were obtained. A cyclohexyl group produced the desired cycloadducts compounds in higher yield than employing *t*-Bu groups. After this report, the Murai group expanded this 3-component reaction with several substituted alkenes instead of ethylene (Scheme 1.19, bottom)[31] They proposed a modified mechanism (Scheme 1.20). The generation of ruthenacycle **A** follows the previous [4+1] cycloaddition reaction mechanism. Then, a 1,2-hydride shift gave the ruthenium hydride complex **B**. Migratory insertion of ethylene and carbon monoxide and reductive elimination generate β-pr opionyl-α,β-unsaturated imine. Following intramolecular

nucleophilic attack of theimine to ketone leads to the intermediate **D**, which undergoes 1,2-ethyl group migration to produce the final product.



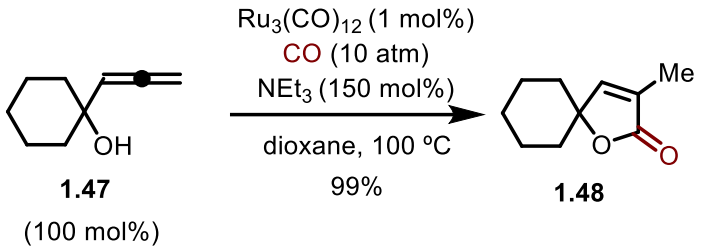
Scheme 1.19 3-Components [4+1] cycloaddition with α,β-unsaturated imine.



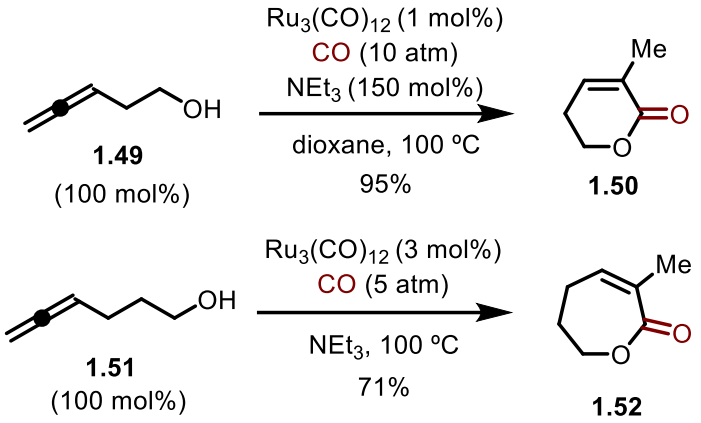
Scheme 1.20 Proposed mechanism of 3-components [4+1] cycloaddition with α,β-unsaturated imine.

Another examples of carbonylative cycloaddition reactions are lactone forming reactions from allenyl alcohol reported by the Takahashi group in 2000. γ-Lactones were obtained after the reaction of 2,3-allenyl alcohol with a catalytic amount of $Ru_3(CO)_{12}$ and trimethylamine as an

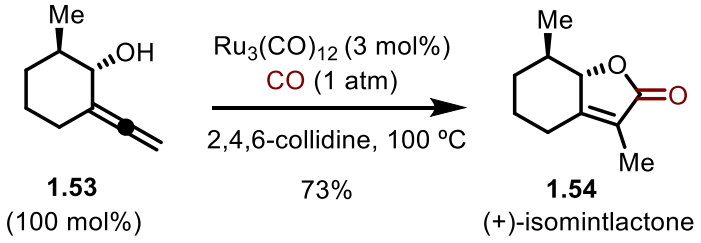
additive under carbon monoxide pressure (scheme 1.21).[32] Furthermore, other allenyl alcohols bearing different chain lengths afforded 6-, 7-membered ring lactones respectively (Scheme 1.22).[33,34] This methodology was successfully applied to the synthesis for (+)-isomintlactone under atomospheric carbon monoxide pressure in short steps (scheme 1.23).[35]



Scheme 1.21 Carbonylative cycloaddition reactions with allenes to form γ-Lactones.

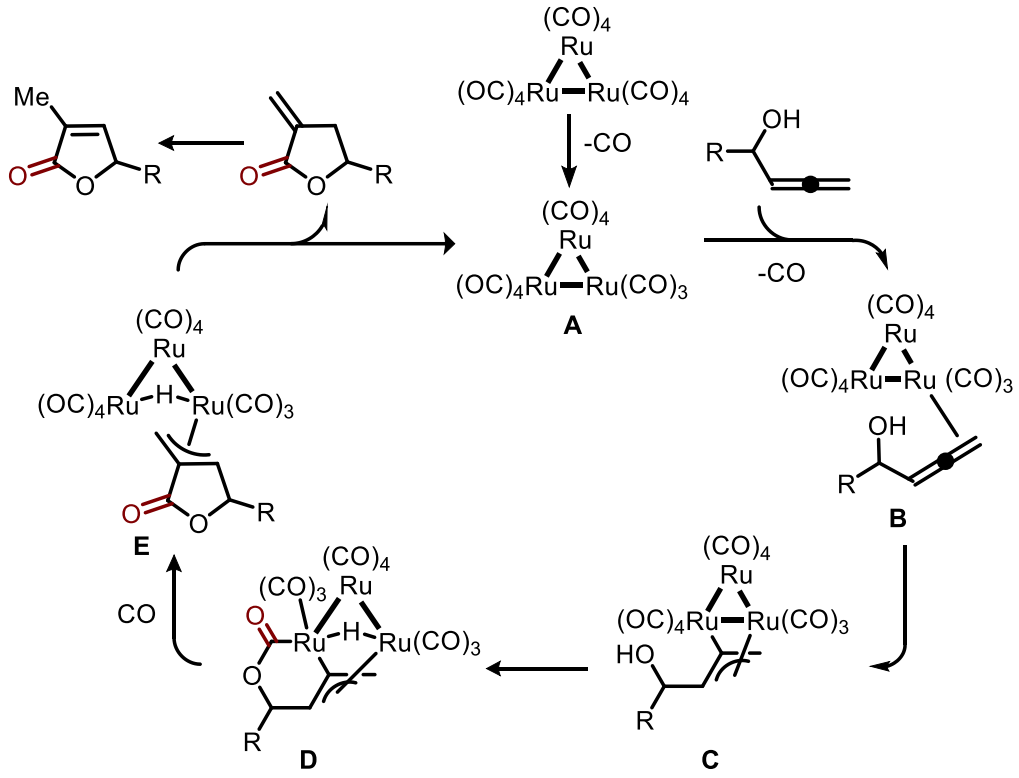


Scheme 1.22 Carbonylative cycloaddition reactions with allenes to form 6-, 7- membered lactones.



Scheme 1.23 Synthesis of (+)-isomintlactone via carbonylative cycloaddition reaction.

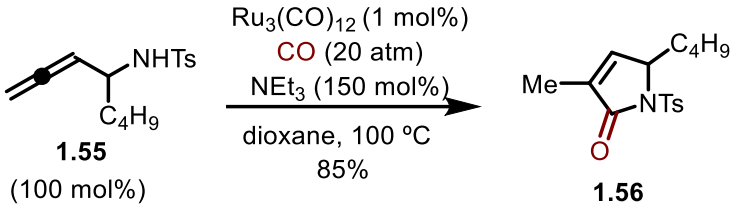
The plausible mechanism is shown in scheme 1.24. Tri-nuclear ruthenium complex coordinates to the allene to form the π-allyl ruthenium complex **C**. Hydrogen transfer from the alcohol to the complex followed by the carbon monoxide insertion and ring closing via reductive elimination to give the lactone with π-allyl ruthenium **E**. The complex proceeds with reductive elimination to produce a terminal alkene, which is isomerized to the more stable final product in the presence of triethylamine.



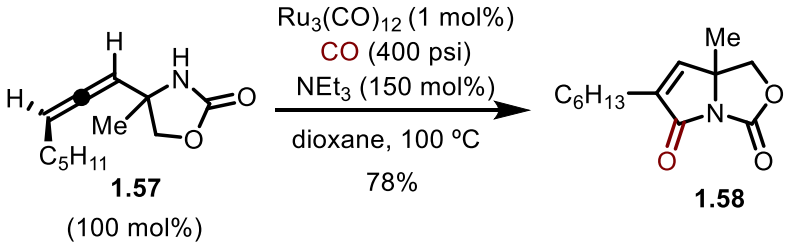
Scheme 1.24 Proposed mechanism of carbonylative cycloaddition reactions with allenes.

In 2001 after this report of lactone synthesis, the Kang group showed that lactams were obtained starting with allenyl amine (Scheme 1.25).[36] The mixture of 2,3-allenyl amines with $Ru_3(CO)_{12}$ catalyst and triethylamine additive under carbon monoxide pressure produced γ-lactams in good to excellent yields. In the same manner, 3,4-allenyl amines furnished δ-lactams. In 2011, the Schomaker group demonstrated the bicyclic lactam forming reaction under similar condition

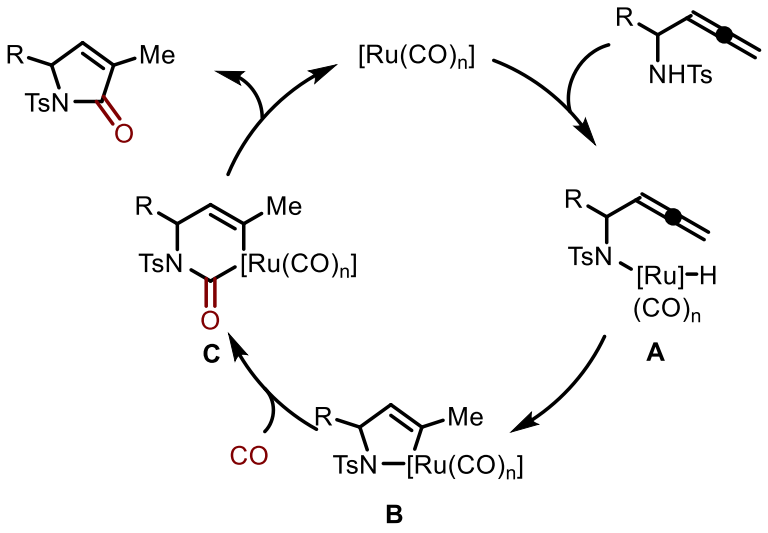
with allenyl carbamate (Scheme 1.26).[37] The proposed mechanism is shown in scheme 1.27. After the coordination of ruthenium to allene, hydrometallation results in the ruthenium complex **B**. Successive carbon monoxide insertion to the sulfonamide side and reductive elimination give the unsaturated lactam.



Scheme 1.25 Carbonylative cycloaddition reactions with allenyl amine.

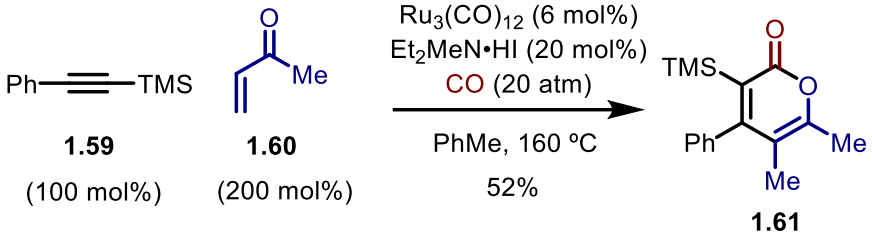


Scheme 1.26 Carbonylative cycloaddition reactions with allenyl carbamate.



Scheme 1.27 Proposed mechanism of carbonylative cycloaddition reactions with allenyl amine.

In 2007, the Ryu group found that vinyl ketones could be used as a three-carbon building block in the reaction (Scheme 1.28).[38] The reaction with alkyne and vinyl ketone under carbon monoxide pressure with $Ru_3(CO)_{12}$ catalyst gave the highly substituted α-pyrones via [3+2+1] cycloaddition. Ammonium salt additive Et_2MeN•HI increased the yield from 20% to 52%.

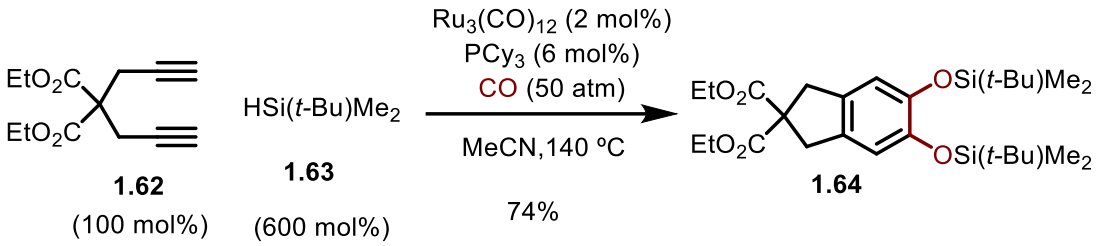


Scheme 1.28 Carbonylative [3+2+1] cycloaddition reactions.

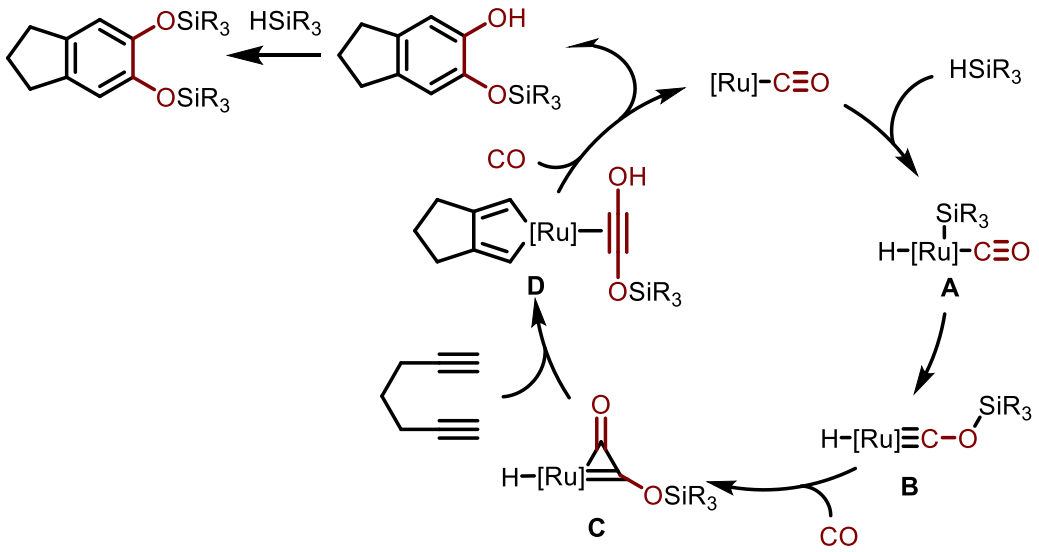
1.2.5 Cycloaddition reactions with two carbon monoxide incorporation

While most of the Ru(0) catalyzed carbonylative cycloaddition reactions integrate one carbon monoxide in the ring system, there are a few examples which assemble two carbon monoxides into the ring. In 1993, Murai reported benzene ring construction by the Ru(0) catalyzed [2+2+1+1] cycloaddition reactions among 1,6-diyne and two carbon monoxides with hydrosilane HSi(*t*-Bu)Me_2 (Scheme 1.29).[5] The reaction of 1,6-diyne with a catalytic amount of $Ru_3(CO)_{12}$ and PCy_3 additive and 6 equivalents of hydrosilane under carbon monoxide pressure at 140 ˚C provided catechol derivatives with two carbon monoxide insertion side by side. When the reaction was conducted with a lower amount of hydrosilane, a mixture of mono- and di- silyl ethers was produced. They also proposed the mechanism (Scheme 1.30). The reaction begins with the generation of a ruthenium hydride complex **A** with hydrosilane. Then, silane migration from

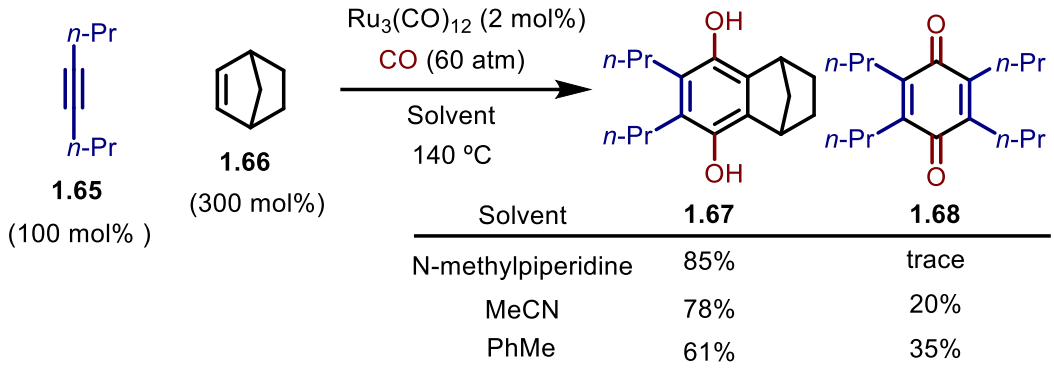
ruthenium center to the oxygen of carbon monoxide resulted in carbine **B**. The next coupling between carbine and carbon monoxide gives the ruthenacyclopropenone intermediate **C** followed by rearrangement and cyclometallation with the diyne to generate complex **D**. It was noted that similar stoichiometric carbyne reactions were known.[39] Subsequent migratory insertion of alkyne resulted in mono silylated benzene derivatives, which is further silylated to give the final products.



Scheme 1.29 Ru(0) catalyzed [2+2+1+1] reaction with carbon monoxide incorporation.

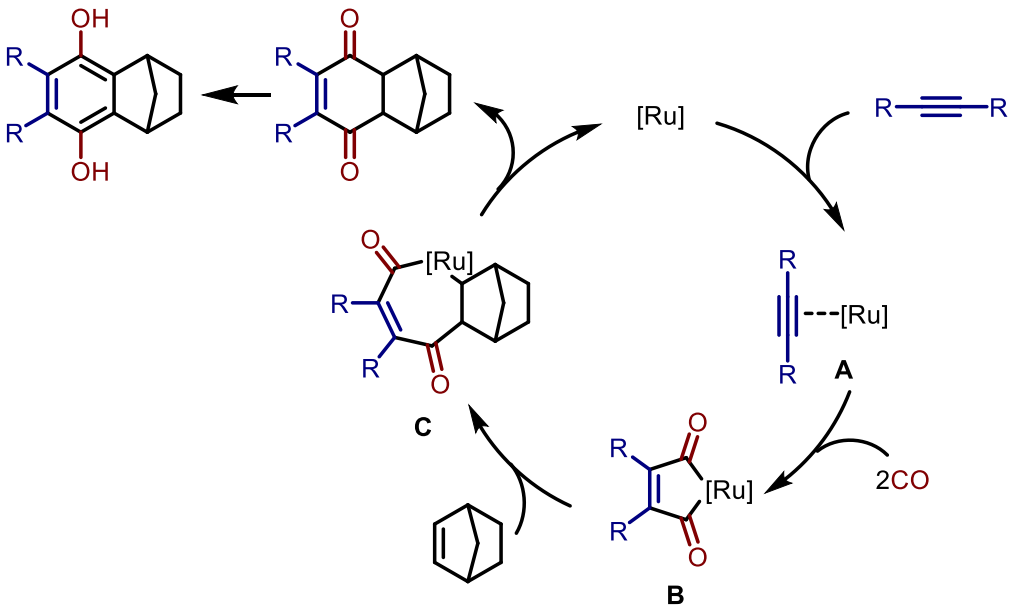


Scheme 1.30 Proposed mechanism of the [2+2+1+1] reaction.



Solvent	1.67	1.68
N-methylpiperidine	85%	trace
MeCN	78%	20%
PhMe	61%	35%

Scheme 1.31 *p*-Hydroquinone synthesis by Ru(0) catalyzed [2+2+1+1] reaction with carbon monoxide.



Scheme 1.32 Proposed mechanism for *p*-hydroquinone synthesis by Ru(0) catalyzed [2+2+1+1] reaction with carbon monoxide.

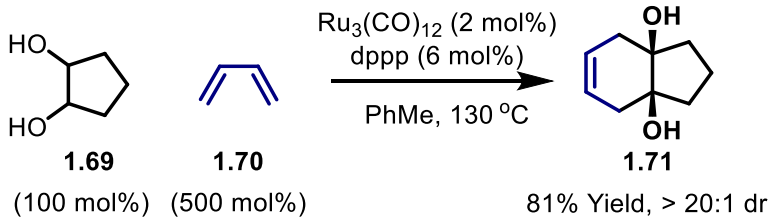
Another example are the cycloaddition reactions assembling two carbon monoxides, one alkyne and one norbornene. The Mitsudo group reported the 4-components carbonylative cycloaddition reactions to form hydroquinone derivatives (Scheme 1.31).[40] The reaction of alkyne and norbornene with the catalytic amount of $Ru_3(CO)_{12}$ under 60 atm of carbon monoxide pressure in N-methylpiperidine gave hydroquinone derivative (**1.67**). In contrast to Murai's previous work, two carbon monoxides were incorporated face to face. The reactions in other solvents such as

toluene or acetonitrile produced quinone byproduct without norbornene incorporation. Other ruthenium catalysts such as $[RuCl_2(CO)_3]_2$ and $[(\eta_6\text{-}C_6H_6)RuCl_2]_2$ were not so effective as $Ru_3(CO)_{12}$. This reaction only worked with norbornene as other alkenes were completely ineffective. The proposed mechanism is shown below (Scheme 1.32). The key intermediate is maleoylruthenium complex **B** produced from alkyne and two carbon monoxides. Then, migratory insertion of norbornene followed by reductive elimination releases quinone, which is isomerized to hydroquinone.

1.3 Cycloadditions reactions with 1,2-diols

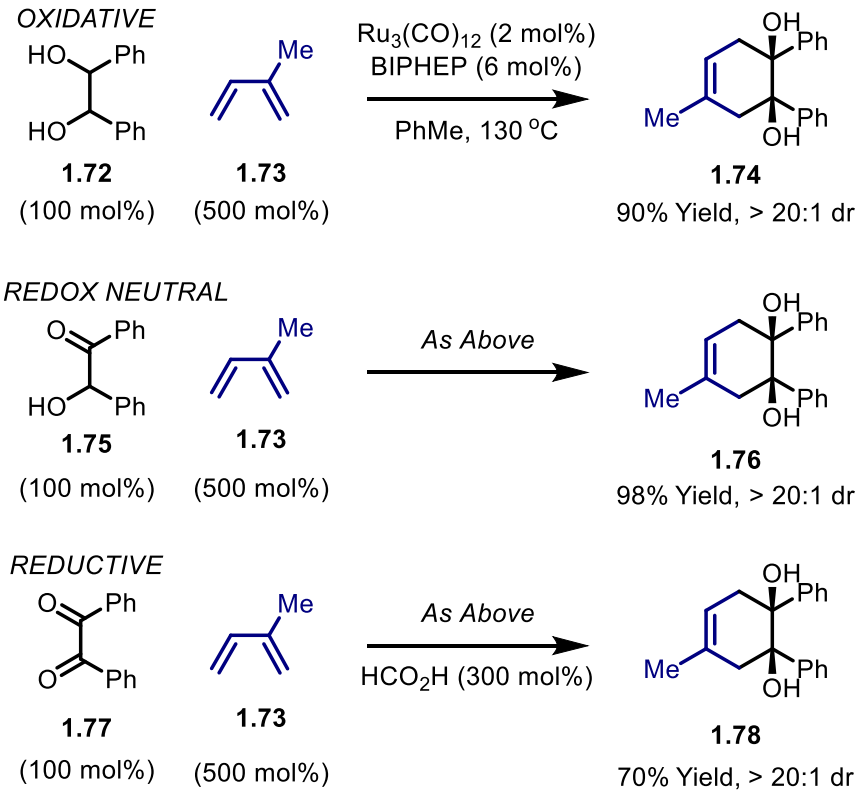
1.3.1 Cycloaddition reactions with alkenes

While hetero Pauson-Khand reaction with ketone reported by Murai[17-19] converted the carbonyl groups into the C-O moieties in lactones under carbon monoxide atmosphere, in 2013 the Krische group found that phosphine-modified zero-valent ruthenium complexes derived from $Ru_3(CO)_{12}$ catalyzed [4+2] cycloaddition reactions between vicinally dioxygenated hydrocarbons (diols, ketols, diones) and 1,3-dienes (Schemes 1.33, 1.34).[41] In contrast to Murai's reactions, a 1,2-dione was incorporated as a C-C component in a cyclohexene ring. The reaction of cyclopentane diol and 1,3-butadiene with a catalytic amount of $Ru_3(CO)_{12}$ and dppp ligand at 130 ˚C gave the [4+2] *cis*-diol cycloadduct in a complete stereoselective manner (**1.71**). Both *cis*- or *trans*-1,2-diols gave the same yield.



Scheme 1.33 Ru(0) catalyzed [4+2] cycloaddition reaction with 1,2-diol.

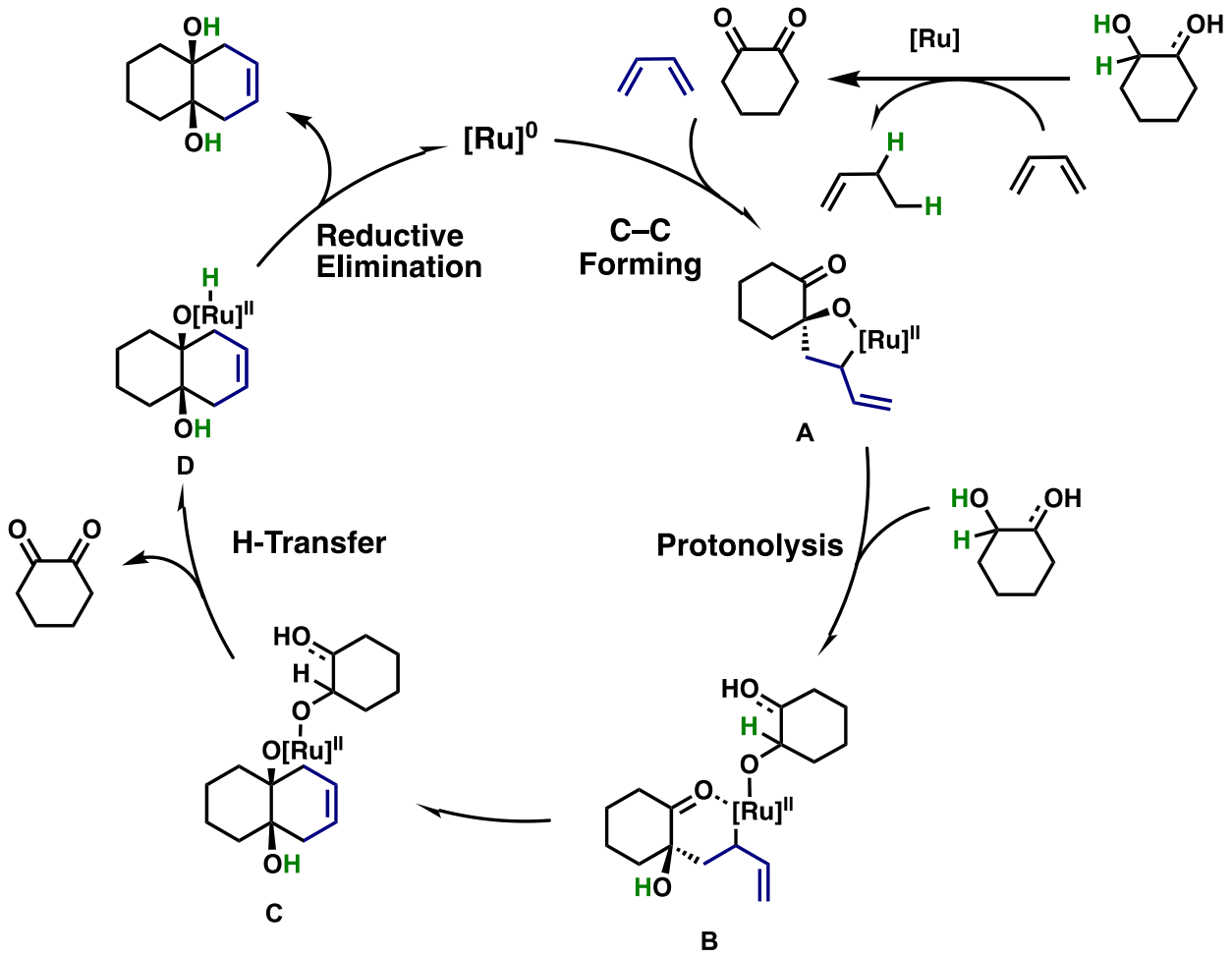
The mechanism is shown in scheme 1.35. 1,3-butadiene and dione derived from diol via hydrogen transfer by ruthenium catalyst[42] give the ruthenacycle complex **A**. Protonolysis occurs with another diol substrate followed by the nucleophilic attack of π-allyl ruthenium to the carbonyl to produce oxo-ruthenium complex **C**. Successive hydrogen transfer and reductive elimination give the final product cyclohexene derivative.



Scheme 1.34 Ru(0) catalyzed [4+2] cycloaddition reaction with 1,2-diol, ketol, or dione.

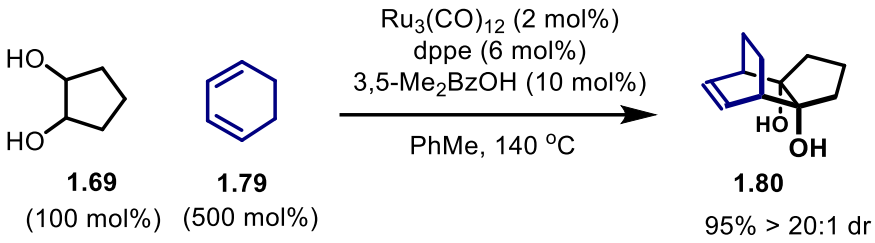
Diol-diene cycloaddition is an oxidative process in which one equivalent of diene is required as hydrogen acceptor. The cycloaddition of α-ketols with dienes occurs under identical conditions and is a redox neutral process. Corresponding reductive cycloadditions of diones with

dienes employing formic acid as terminal reductant have also been developed. Thus, ruthenium catalyzed cycloaddition may be conducted from the diol, ketol or dione oxidation levels (Scheme 1.34).



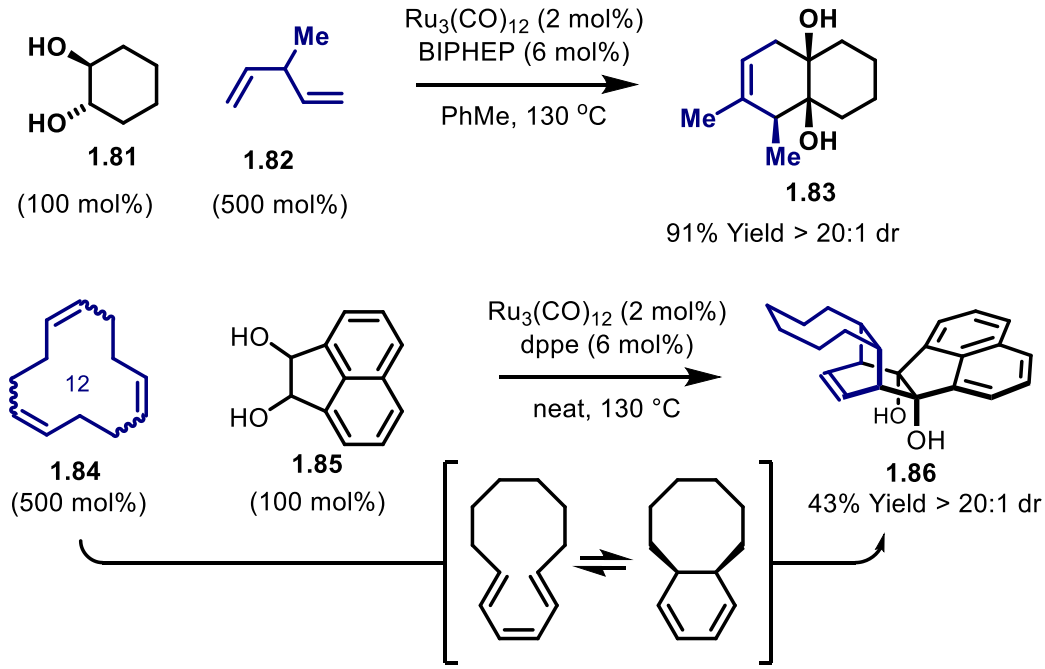
Scheme 1.35 Proposed mechanism of [4+2] cycloaddition reaction with 1,2-diol.

The diol-mediated cycloaddition of cyclohexadiene enabled access to bridged carbocycles (Scheme 1.36).[43] The reaction of cyclopentane diol and 1,3-cyclohexadiene with a catalytic amount of $Ru_3(CO)_{12}$, dppe, and 3,5-dimethyl benzoic acid at 140 ˚C afforded the bridged carbocycle diol in complete *cis*-diol and *exo*- selectivities.



Scheme 1.36 Ru(0) catalyzed [4+2] cycloaddition reaction with cyclohexadiene.

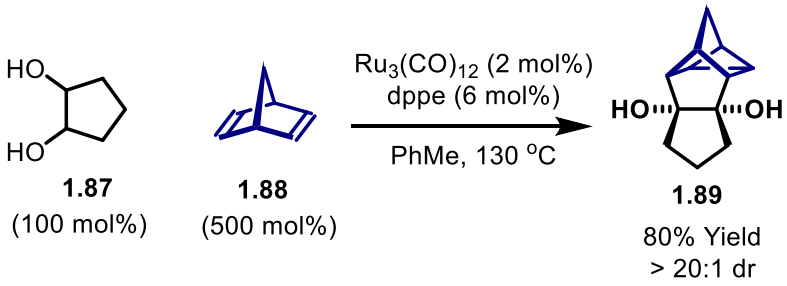
The ability of $Ru_3(CO)_{12}$ to catalyze olefin isomerization[44] enabled recruitment of non-conjugated dienes in diol-mediated [4+2] cycloaddition with efficiencies roughly equivalent to that observed for the corresponding conjugated dienes (Scheme 1.37, top). A remarkable application of tandem olefin isomerization-cycloaddition was found in the reaction of 1,5,9-cyclododecatriene. A transient 1,3,5-triene was formed that exists in equilibrium with the



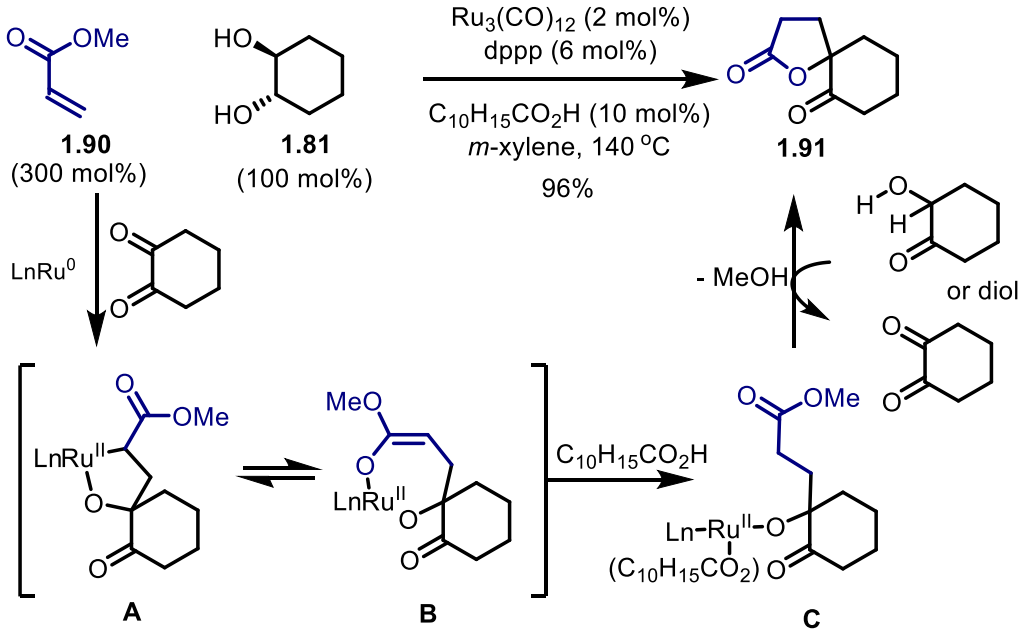
Scheme 1.37 Cycloaddition with diols and non-conjugated alkene via isomerization.

corresponding diene-containing [6.4.0] tricycle, which was converted to the indicated bridged polycycle as a single diastereomer.

They also reported ruthenium catalyzed [2+2+2] *homo*-Diels-Alder reactions[45,46] between diols and norbornadiene (Scheme 1.38). The reaction of cyclopentane diol and norbornadiene with a catalytic amount of $Ru_3(CO)_{12}$ and dppe at 130 ˚C gave the cycloadduct diol (**1.89**) in complete *cis*-diol and *exo*- selectiviteis.



Scheme 1.38 Ru(0) catalyzed [4+2] cycloaddition reaction with norbornadiene.

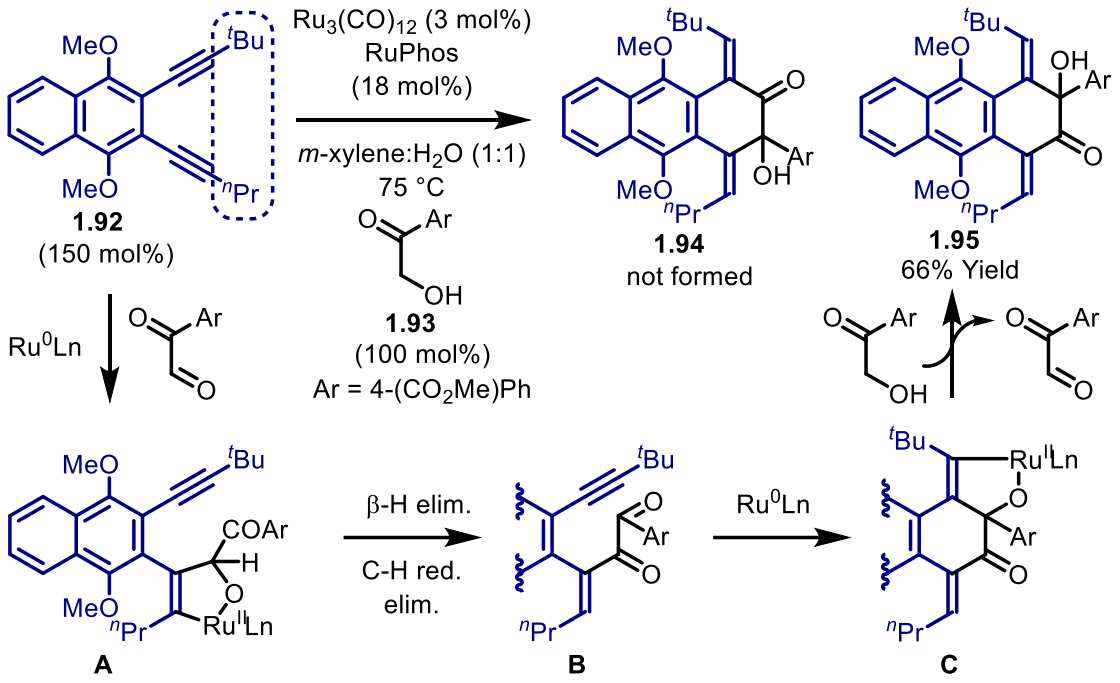


Scheme 1.39 Ru(0) catalyzed γ-lactones synthesis from diol.

While Murai reported lactone synthesis with ketones under carbon monoxide, the Krische group developed a new methodology to access γ-lactones from diols and α,β-unsaturated esters without carbon monoxide (Scheme 1.39).[47] The reaction of a diol and α,β-unsaturated esters with a catalytic amount of $Ru_3(CO)_{12}$, dppp, and 10 mol% 1-adamantane carboxylic acid at 140 ˚C gave spiro- and α-methylene-γ-butyrolactones. This reaction was also effective with hydroxy-2-oxindole with KO*t*-Bu additive instead of 1-adamantane carboxylic acid. This reaction was thought to begin with oxidative cyclometallation between α,β-unsaturated esters and dione derived from diol starting material after hydrogen transfer. Then protonolysis of ruthenacycle **B** promoted by acid additive produces ester **C**, which is readily cyclized leaving methanol to give the final product.

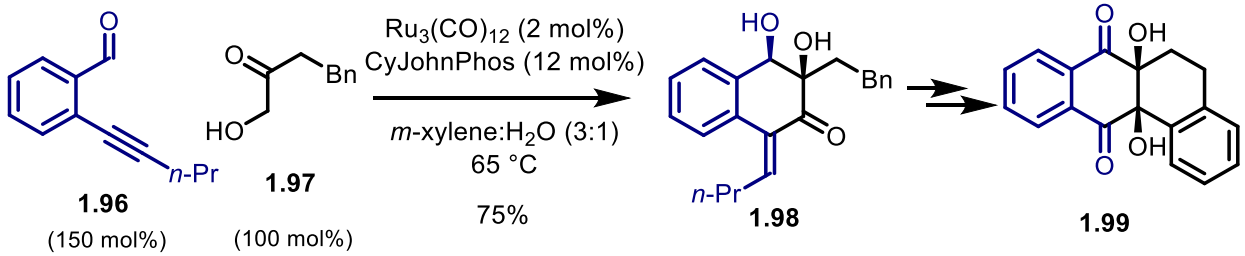
1.3.2 Cycloaddition reactions with alkynes

It was known that same reaction system allowed C-C bond formation between diol and alkyne.[48] The Krische group applied that reaction to ring forming transformations starting with 1,5-diynes (Scheme 1.40).[49] The reaction of a 1,5-diyne and ketol with a catalytic amount of $Ru_3(CO)_{12}$, Ruphos as ligand, and 10 mol% 1-adamantane carboxylic acid at 75 ˚C in mixture of *m*-xylene and water gave a [4+2] diene cycloadduct. To suppress alkyne reduction, the reaction was conducted in a redox-neutral manner from the ketol oxidation level rather than using diol reactants, which required a sacrificial hydrogen acceptor. The cycloadditions proceeded at relatively low temperatures in aqueous organic media. Ruthenium(0)-mediated alkyne-carbonyl oxidative coupling occurs initially at the less sterically demanding *n*-propyl substituted alkyne. After a second oxidative coupling at the *t*-butyl substituted alkyne and transfer hydrogenolysis of the resulting oxaruthenacycle, the cycloadduct is obtained as a single constitutional isomer.

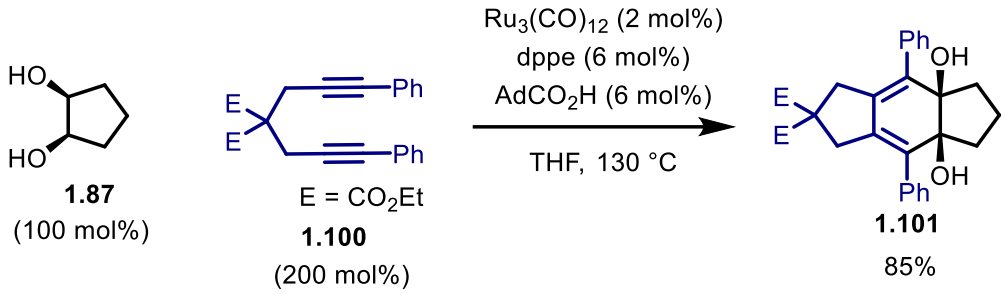


Scheme 1.40 Ru(0) catalyzed reactions with 1,5-diyne and ketol.

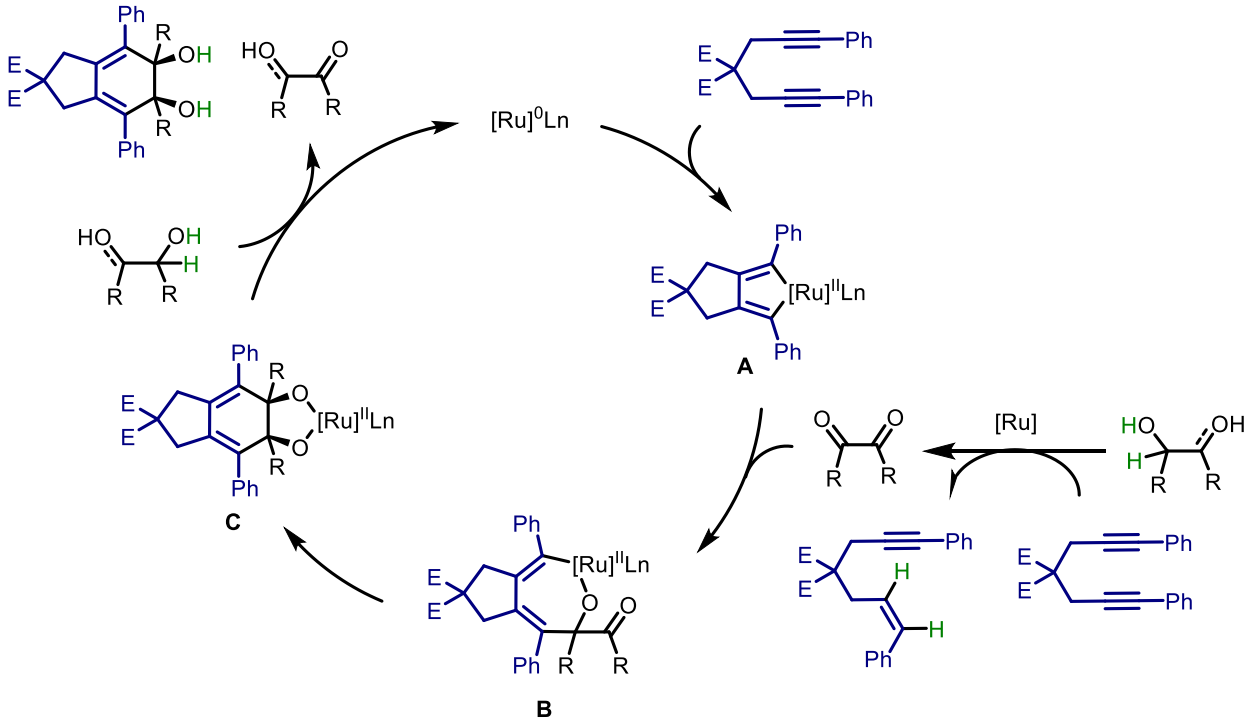
They also reported a similar ring forming reaction with *ortho*-acetylenic benzaldehydes instead of 1,5-diynes in which alkyne-carbonyl oxidative coupling occurred followed by aldehyde-dione oxidative coupling (Scheme 1.41).[50] The cycloadduct products were converted into tetracyclic naphthoquinones bearing diols, whose structures are seen in many angucycline natural products.



Scheme 1.41 Ru(0) catalyzed reactions with alkyne-carbonyl and ketol.



Scheme 1.42 Ru(0) catalyzed reactions with1,6-diyne.

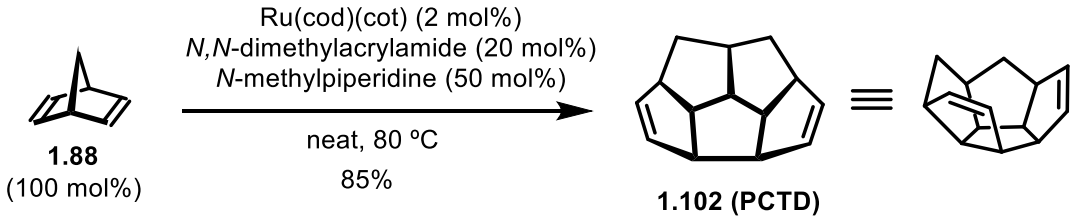


Scheme 1.43 Proposed mechanism of Ru(0) catalyzed reactions with 1,6-diyne.

Metal catalyzed [2+2+2] cycloadditions with alkynes enable convergent construction of (poly)cyclic molecules from π-unsaturated reactants.[51] The Krische group found that a ruthenium(0) catalyst allowed diols to proceed those cycoaddition reactions.[52] The reaction of 1,6-diynes and diols with a catalytic amount or $Ru_3(CO)_{12}$ and dppe ligand with an acid additive at

130 ˚C delivered the *cis*-diol diene cycloadducts (Scheme 1.42). 1,6-Diynes that are unsubstituted at the acetylenic terminus and 1,7-diynes are not efficient partners for cycloaddition. The proposed mechanism was shown in scheme 1.43. The dione derived from diol via hydrogen transfer would be inserted into the ruthenium cyclopentadiene **A** to form oxo-ruthenium intermediate **B**. Successive second carbonyl insertion resulted in the *cis*-dioxo-ruthenium complex **C**, which gave the final cycloadduct after hydrogen transfer and reductive elimination.

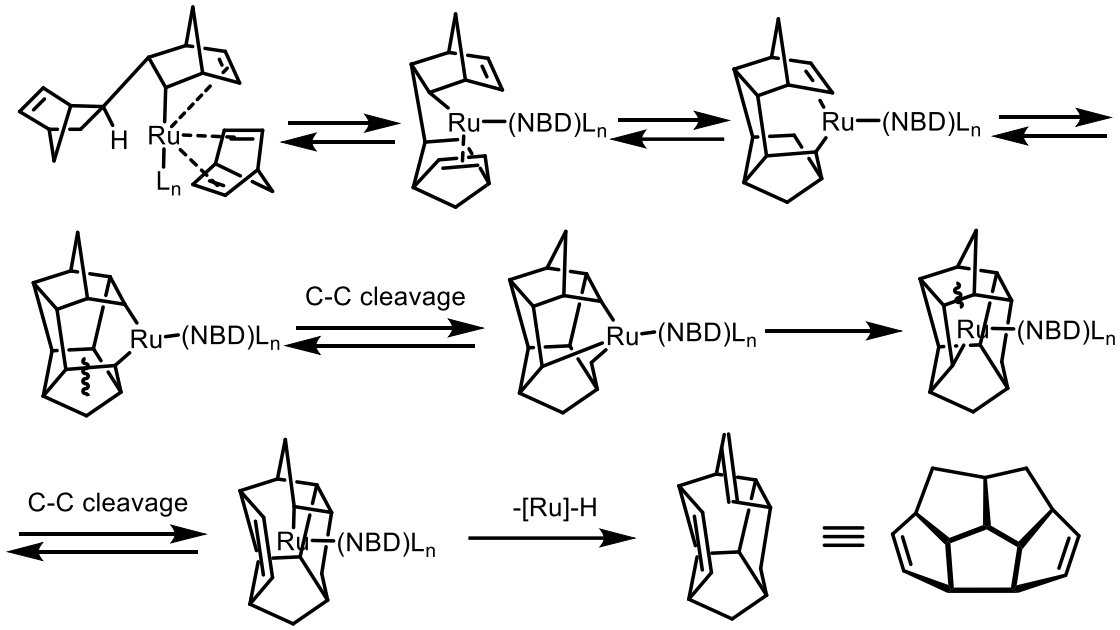
1.4 Cycloaddition reactions via C-C bond cleavage



Scheme 1.44 Ru(0) catalyzed dimerization and reconstruction via C-C bond cleavage.

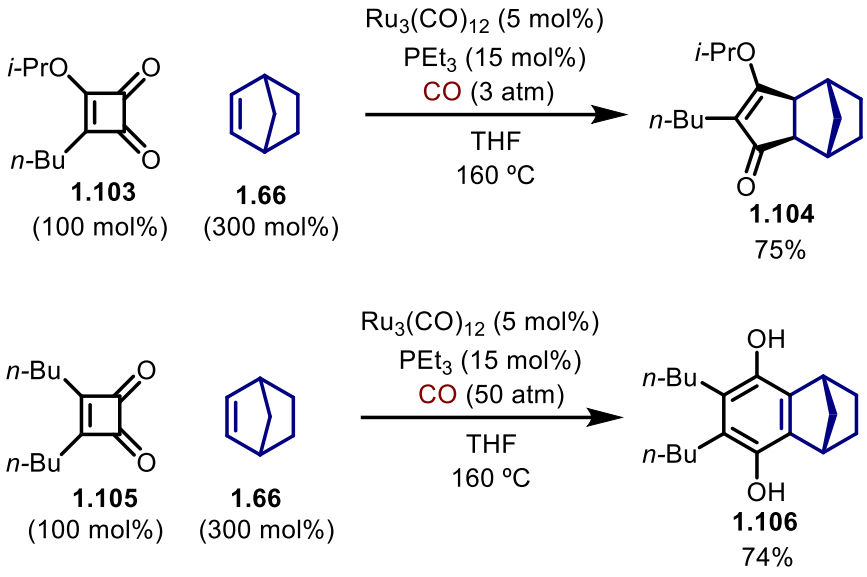
Transition metal catalyzed functionalization reactions via C-C bond cleavage[53] has been emerging as insertion of various functional groups into C-C bonds realize new synthetic approaches to access the targeted molecules. The first C-C cleavage with zerovalent ruthenium catalyst was observed by Mitsudo *et al* in 1994 (Scheme 1.44).[8] The reaction with Ru(cod)(cot) catalyst with norbornadiene with *N,N*-dimethylacrylamide and *N*-methylpiperidine additives produced novel pentacyclo[5.4.$2^{1.7}$.$1^{3.6}$.$0^{10.13}$.$0^{12.14}$]tetradeca-4,8-diene (PCTD), which was confirmed by X-ray analysis. The reaction was sensitive to the reaction conditions, and *N,N*-dimethylacrylamide was crucial. Although the reaction mechanism was not so clear, the structure clearly showed C-C cleavage process occurred during dimerization. In their following study, they proposed a mechanism via multiple C-C cleavages (Scheme 1.45).[54] The reaction begins with

dimerization of norbornadienes. Subsequent intramolecular alkene insertions and C-C cleavages to release the ring strains result in the PCTD after β-hydride elimination as shown in the scheme.

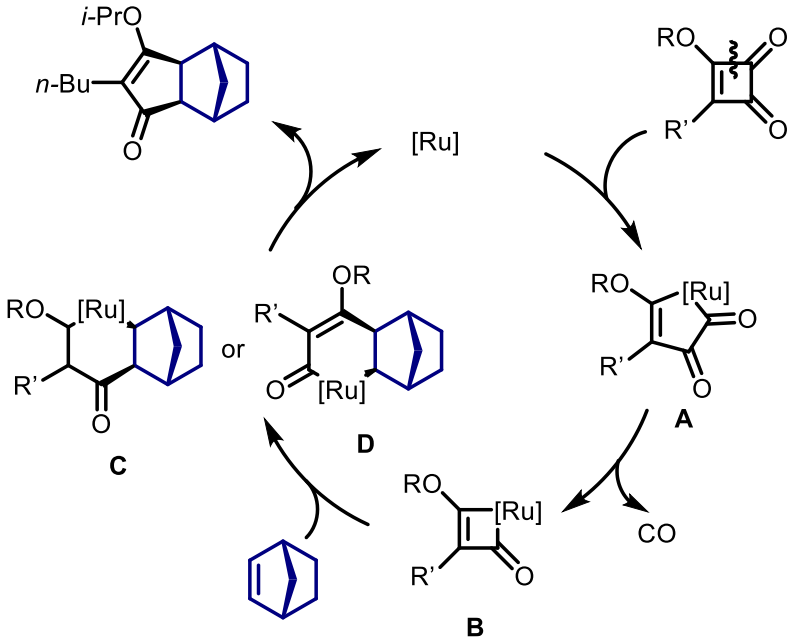


Scheme 1.45 Proposed mechanism of PCTD synthesis by Ru(0) catalyst.

In 2000, the Mitsudo group found that a Ru(0) catalyst was able to cleave the C-C bond of cyclobutedione, and insert alkene to the ruthenacycleto followed by the cycloadduct production. [55] Treatment of 4-butyl-3-isopropoxycyclobut-3-ene-1,2-dione with norbornene in the presence of $Ru_3(CO)_{12}$ catalyst and PEt_3 ligand under carbon monoxide pressure at 160 ˚C gave the cyclopentenone derivative in complete diastereoselectivity (Scheme 1.46). The reaction without PEt_3 was ineffective. Other phosphines such as PBu_3, PCy_3, PPh_3, dppe, and dppp only give the products in moderate yield. Higher carbon monoxide pressure suppressed decarbonylation to furnish the corresponding hydroquinone via [4+2] cycloaddition. The scope of the alkene was quite



Scheme 1.46 Cycloaddition reactions with cyclobutedione via C-C bond cleavage.

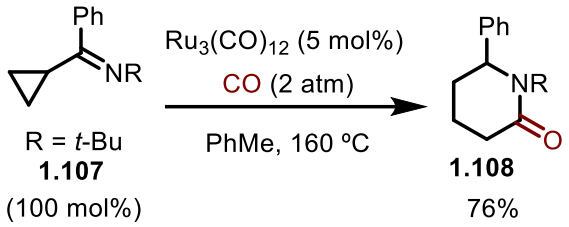


Scheme 1.47 Proposed Mechanism of cycloaddition reactions with cyclobutedione via C-C bond cleavage.

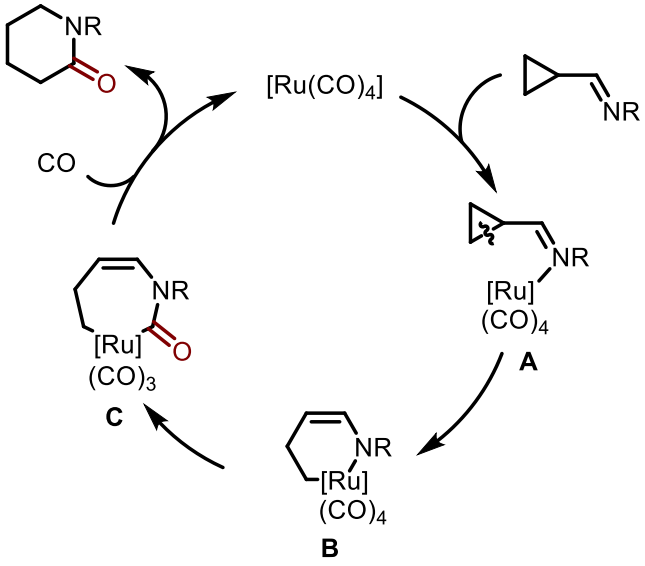
limited only to norbornene and ethylene. The proposed mechanism was shown in scheme 1.47.

The oxidative addition to cyclobutedione at C2-C3 position would produce the ruthenium complex

A. Under low carbon monoxide pressure decarbonylation occurs to form ruthenacyclobutenone **B**, into which norbornene is inserted to give the intermediate **C** or **D**. Successive reductive elimination affords the final cyclopentenone derivative.



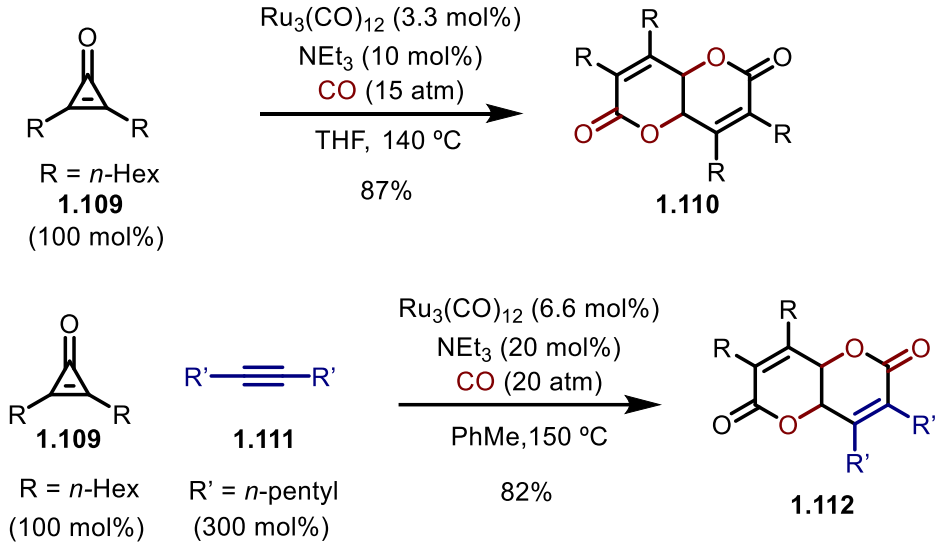
Scheme 1.48 [5+1] Cycloaddition reaction with cyclopropyl imine and carbon monoxide**.**



Scheme 1.49 Proposed mechanism of [5+1] Cycloaddition reaction.

In 2000, the Murai group reported the Ru(0) catalyzed [5+1] cycloaddition reactions via C-C bond cleavage of cyclopropyl ring.[56] The reaction of the cyclopropyl imine with carbon monoxide using a $Ru_3(CO)_{12}$ catalyst at 160˚C gave the corresponding γ-lactam in moderate to

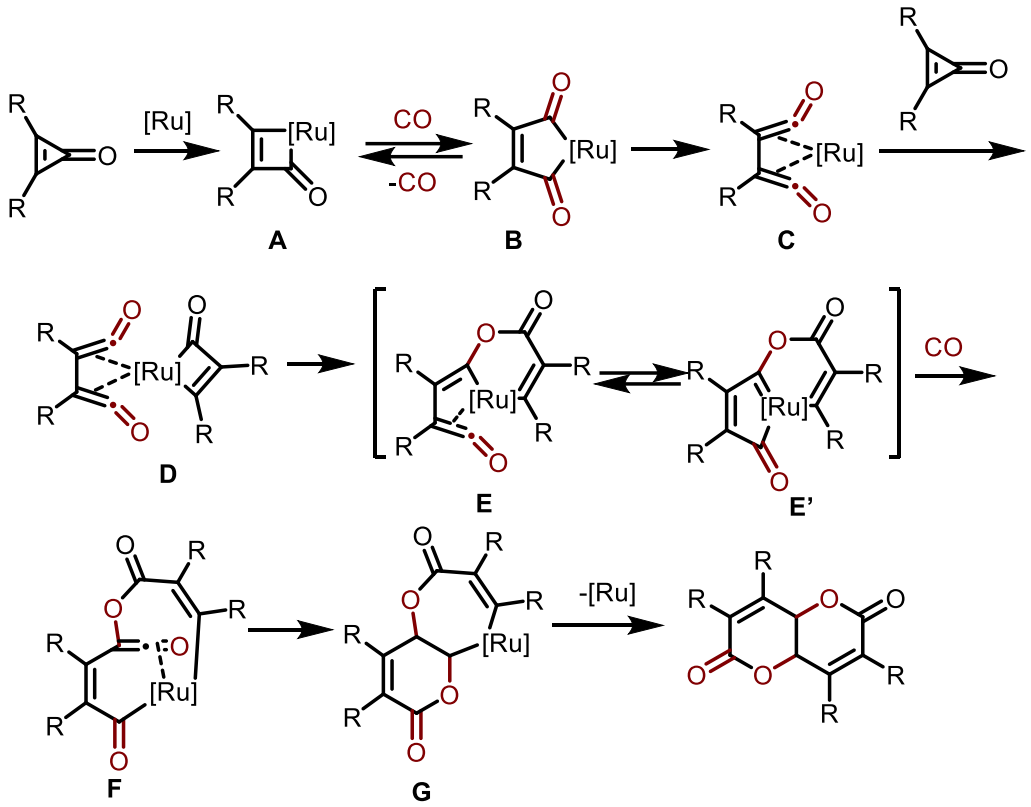
good yield (Scheme 1.48). The yield was highly dependent on the substituent group on the nitrogen. Only *t*-Bu or cyclohexyl gave the cycloadducts in sufficient yield. The reaction starts with the coordination of ruthenium to the imine (Scheme 1.49). Thanks to the proximity effect of the imine directing group, oxidative addition into cyclopropyl ring leads to the aza-ruthenacycle. Subsequent carbon monoxide insertion and reductive elimination furnishes the lactam.



Scheme 1.50 Ru(0) catalyzed cycloaddition reaction with cyclopentenone and carbon monoxide.

In 2002, the Mitsudo group found that cyclopropenones were also applicable to Ru(0) catalyzed cycloaddition reactions as three carbons building blocks via C-C bond cleavage.[57] The reaction of cyclopropenone with a catalytic amount of $Ru_3(CO)_{12}$ and triethylamine additive under carbon monoxide pressure at 140˚C provided the corresponding pyranopyranodione. Addition of triethylamine dramatically suppressed the dimerization of cyclopropenones. When the alkyne was carried out in the reaction, both of alkyne and cyclopropenone were inserted in 1:1 ratio. They proposed the plausible mechanism based on ^{13}C labelling results (Scheme 1.51). Oxidative

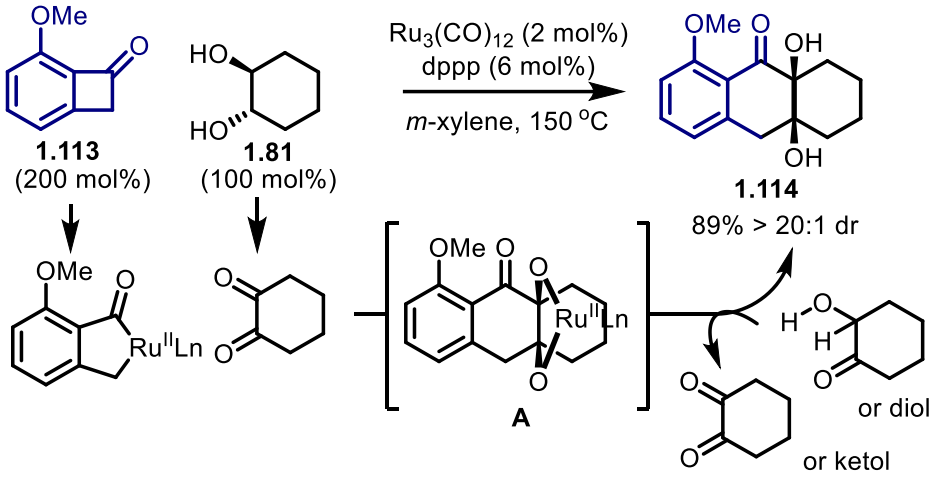
addition to cyclopentenone and insertion of carbon monoxide gives the maleoylruthenium intermediate **B**. Then, second oxidative addition to another cyclopentenone followed by migratory insertion to ketene and tautomerization lead to the ruthenium carbene intermediate **E'**. Another carbon monoxide insertion and migratory insertion to the ketene result in the ruthenium complex **F**, which finally give the final product after reductive elimination.



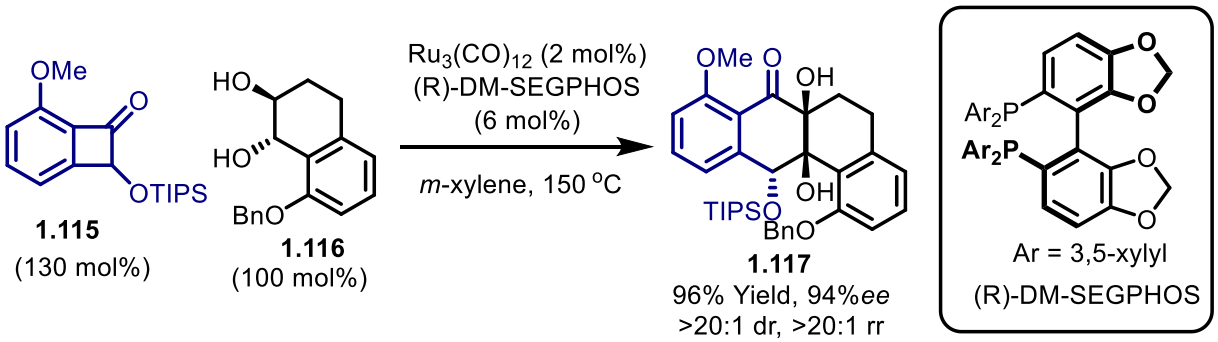
Scheme 1.51 Proposed mechanism of Ru(0) catalyzed cycloaddition reaction with cyclopentenone and carbon monoxide.

In 2017, the Krische group reported Ru(0) catalyzed [4+2] cycloaddition reaction with cyclobutanone via C-C bond cleavage (Scheme 1.52).[58] Treatment of the benzocyclobutanone and diol with a catalytic amount of $Ru_3(CO)_{12}$ and dppp ligand at 150˚C provided the corresponding

[4+2] cycloadduct in complete *cis*-diol diastereoserectivity. In the next year, they succeeded to develop the enantioselective reaction with a chiral phosphine ligand (1.53).[59]



Scheme 1.52 [4+2] Cycloaddition reaction with benzocyclobtanone via C-C cleavage.

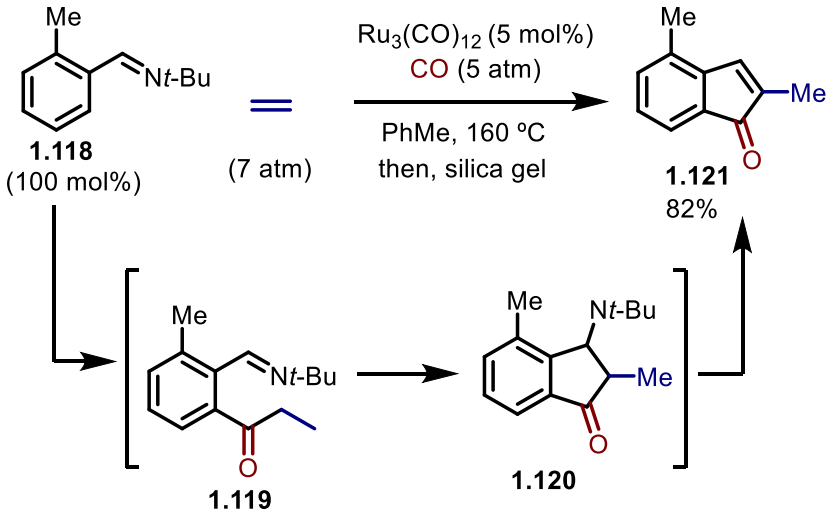


Scheme 1.53 Enantioselective [4+2] Cycloaddition reaction with benzocyclobtanone.

1.5. Cycloaddition reactions via C-H activation

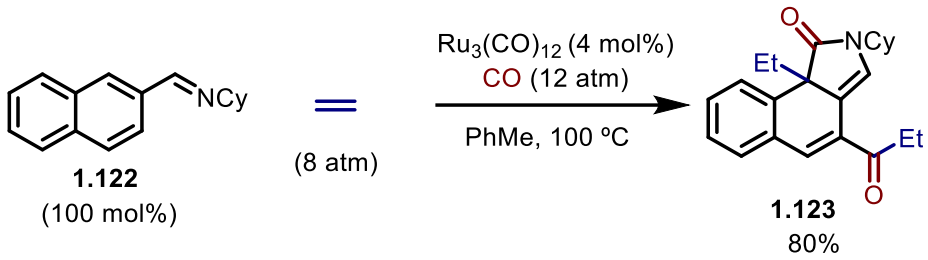
Transition metal catalyzed C-H activation reactions[60] are the direct functionalization methodologies in which metal insert into conventionally inactive bonds, for examples aromatic sp_2 C-H and sp_3 C-H on a simple alkyl chain, and introduce functional groups via reductive

elimination. Because these reactions allow access to a broad range of compounds which were difficult to synthesize in conventional methods, they have been intensively studied by many scientists. The first ring forming reaction via Ru(0) catalyzed C-H activation was demonstrated by the Murai group in 1997.[61] The reaction of benzylidene amine with $Ru_3(CO)_{12}$ catalyst under ethylene and carbon monoxide pressure followed by silica gel addition and stirring for 1 day at ambient temperature produced the corresponding indenone in one pot (Scheme 1.54). Substituents on the benzene ring at the *o*-, or *m*- position is necessary to prevent double carbonylation. The first step of this reaction is coordination of ruthenium to the imine followed by C-H bond cleavage. Then, insertion of ethylene and carbon monoxide, and successive reductive elimination leads to propionation. The propionated products readily undergo intramolecular aldol condensation, which was isolable after the reaction. Silica gel addition promotes the elimination of *t*-Bu amine to give solely the indenone.



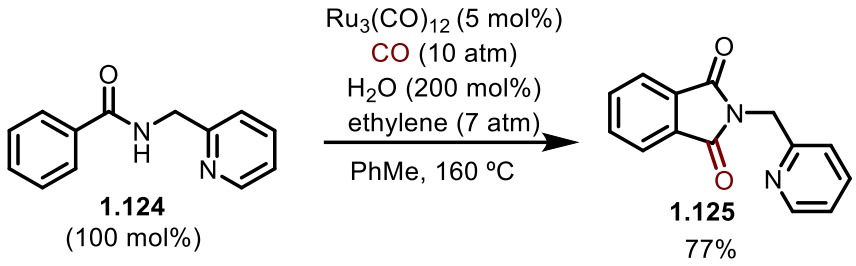
Scheme 1.54 Indenone synthesis by Ru(0) catalyzed ring forming reaction via C-H activation.

In 2000, the Imhof group reported lactam synthesis via carbonylative C-H activation (Scheme 1.55).[62] The treatment of napthylaldimine with a catalytic amount of $Ru_3(CO)_{12}$ under ethylene and carbon monoxide for 1.5 hours gave the corresponding lactam with ethyl group insertion. In the shorter reaction time the propionated product at C2 position was obtained as the major product with no observation of the one at C1 position. It is reasonable that the less hindered *o*-position was favorably produced. The reaction mechanism was thought to be same with the previous studies.[30,31]



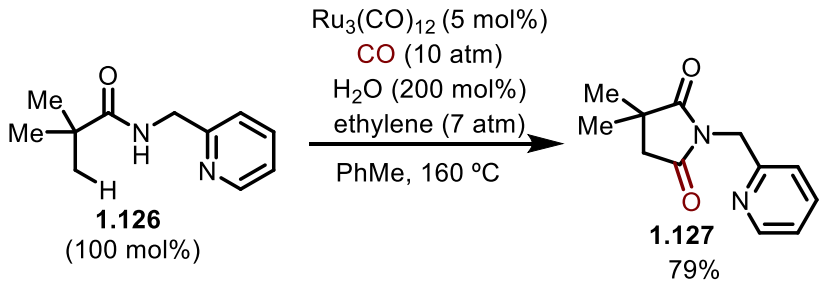
Scheme 1.55 Lactam synthesis by Ru(0) catalyzed cycloaddition reaction via C-H activation.

In 2009, the Chatani group reported Ru(0) catalyzed carbonylative cycloaddition via C-H activation utilizing bidentate directing group (Scheme 1.56).[63] The reaction of the amide bearing pyridin-2-ylmethylamine moiety with a catalytic amount of $Ru_3(CO)_{12}$ under ethylene and carbon monoxide and water at 160 ˚C gave the phthalimide in good yield. While previously reported reactions by Murai and Imhof incorporated ethylene, in this reaction ethylene just worked as a hydrogen acceptor. Without H_2O, the reaction yield severely dropped to 25%. H_2O might work to generate catalytically active ruthenium species. The hydrogen acceptor was also crucial in the reaction. Other alkene hydrogen acceptors such as norbornene or methyl acrylate were ineffective.

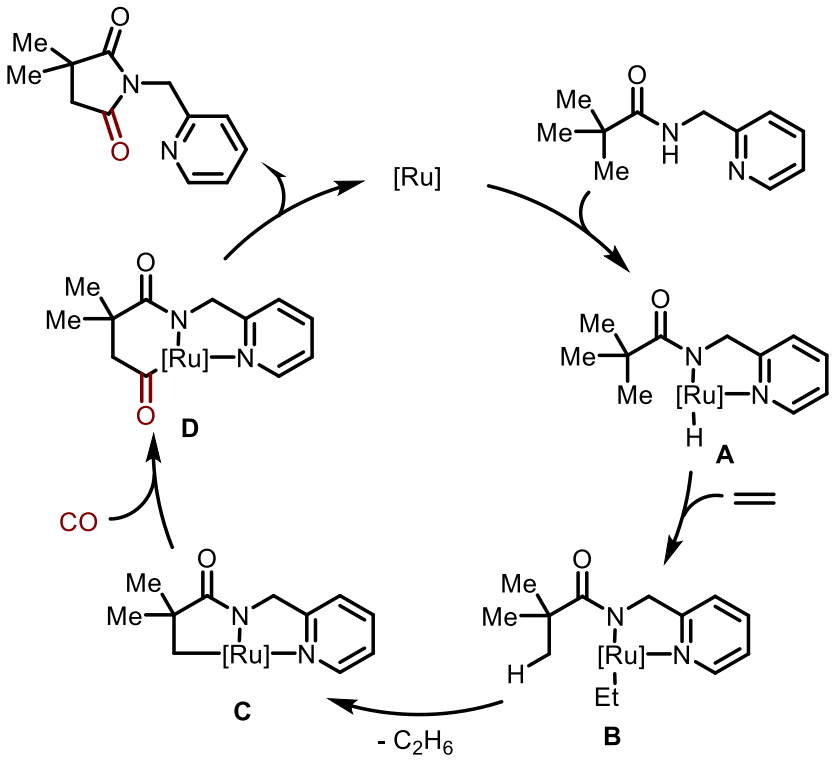


Scheme 1.56 [4+1] cycloaddition reaction with carbon monoxide via aromatic sp_2 C-H activation.

Later in 2011, the same group found that Ru(0) catalyst was able to cleave inactive sp_3 C-H bonds (Scheme 1.57).[64] The reaction of the amide with bidentate directing group under the same conditions for 5 days with the previous report gave the succinimide through sp_3 C-H bond activation. Kinetic isotope effect (KIE) experiments with a deuterated methyl group suggested that C-H activation step was the rate-determining step. The proposed mechanism was shown in scheme 1.58. Ruthenium catalyst would be strongly bound to the bidentate ligand. Insertion of ethylene and C-H activation of the methyl C-H followed by reductive elimination to release ethane resulted in the ruthenium complex **C**. Next carbonmonoxide insertion and reductive elimination gave the corresponding succinimide.

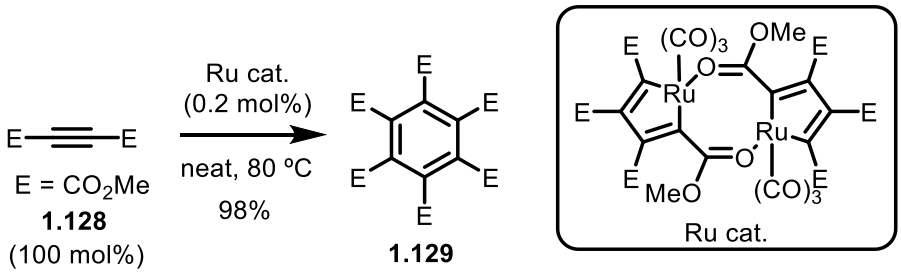


Scheme 1.57 [4+1] cycloaddition reaction with carbon monoxide via sp_3 C-H activation.



Scheme 1.58 Proposed mechanism of [4+1] cycloaddition reaction with carbon monoxide via sp_3 C-H activation.

1.6 [2+2+2] Cycloaddition reactions

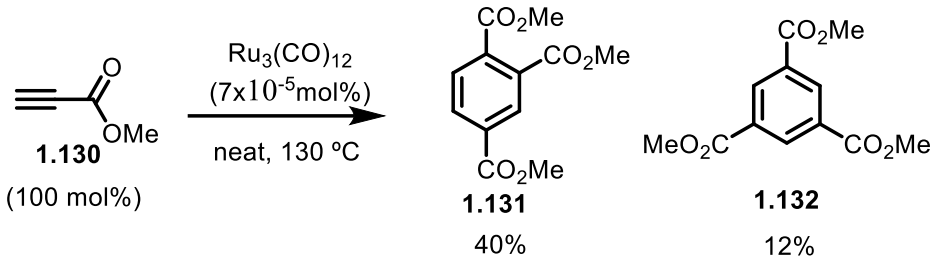


Scheme 1.59 [2+2+2] cycloaddition reaction with precatalyst derived from $Ru_3(CO)_{12}$.

While stoichiometric [2+2+2] cycloaddition reactions with Ru(0) complex was known in 1978,[65] the catalytic reaction was not reported until 1989. The Lindner group used the ruthenium

precatalyst derived from (η^2-C_2H_4)$Ru(CO)_4$ for the catalytic [2+2+2] cycloaddition reactions with activated alkyne (scheme 1.59).[66] The reaction of acetylenedicarboxylic acid dimethyl ester with a catalytic amount of the ruthenium precatalyst at 80 ˚C gave the cyclotrimerzied benzene derivative in quantitative yield.

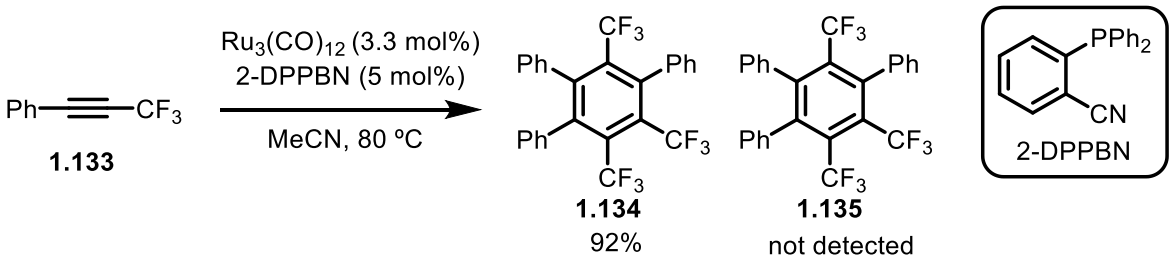
In 1990, during the course of dimerization of methyl acrylate, the Lau group found $Ru_3(CO)_{12}$ was capable of cyclotrimerization reactions.[67] The reaction of methyl propionate with small amount of $Ru_3(CO)_{12}$ loading at 130 ˚C produced the regioisomeric mixture of benzene derivatives (Scheme 1.60). While activated electron deficient alkyne gave the trimerized products, phenyl acetylene was ineffective.



Scheme 1.60 [2+2+2] cycloaddition reaction of methyl propionate with $Ru_3(CO)_{12}$ catalyst.

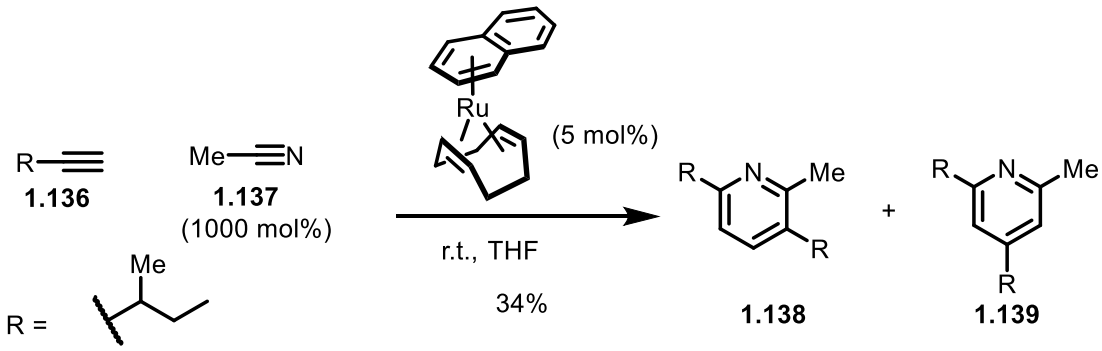
In 2011, the Itoh group disclosed the excellent reactivity of $Ru_3(CO)_{12}$ with trifluoro substituted alkynes (Scheme 1.61).[67] The treatment of trifluoromethylated internal alkyne with a catalytic amount of $Ru_3(CO)_{12}$ and 2-(diphenylphosphino)benzonitrile (2-DPPBN) ligand at 80 ˚C provided the 1,2,4-substituted benzene derivative in complete regioselective manner in excellent yield. Without 2-DPPBN or with other ligand such as PPh_3 or dppe resulted in poor yields and moderate regioselectivities. While trifluoro alkynes with aryl substituents bearing electron withdrawing group showed excellent reactivity, *p*-$OMeC_6H_4$ completely shut down the reaction. Generally speaking, alkyne scopes were severely narrow in Ru(0) catalyzed [2+2+2] reactions.

The Berry group noted bis(imino)pyridine ruthenium(0) complex showed poor catalytic reactivity to form benzene with acetylene although they didn't provide detailed reaction conditions.[68]



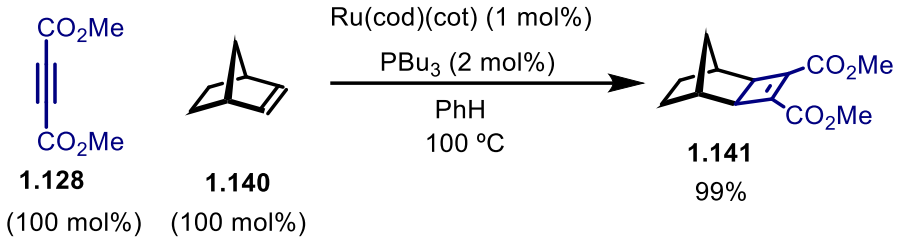
Scheme 1.61 [2+2+2] cycloaddition reaction of trifluoromethyl alkynes.

The synthesis of pyridine derivatives as well as benzene derivatives was also known. In 1998, the Bennett group showed that the Ru(0) arene complex catalyzed [2+2+2] cycloaddition reaction afforded the pyridine derivatives in moderate turn over numbers (Scheme 1.62).[69] The reaction of terminal alkyne with a catalytic amount of [Ru(η^6-naphthalene)(cod)] and excess acetonitrile at ambient temperature gave the mixture of the regioisomers in moderate yield.

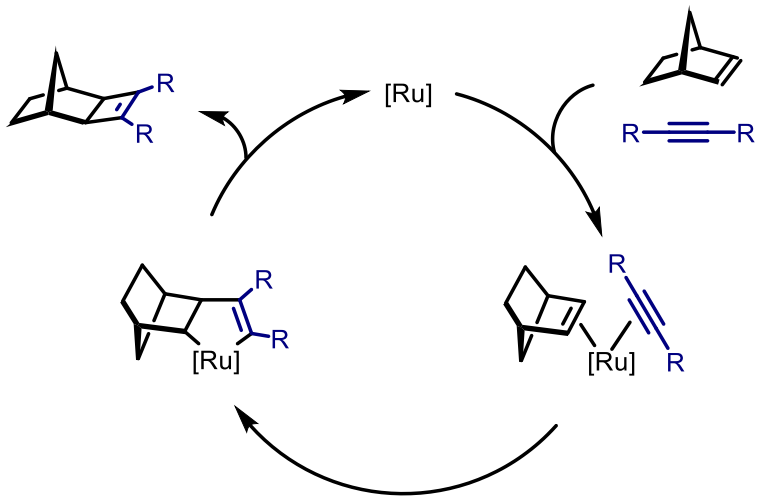


Scheme 1.62 Pyridine synthesis via [2+2+2] cycloaddition reaction.

1.7 [2+2] Cycloaddition Reactions



Scheme 1.63 Ru(0) catalyzed [2+2] cycloaddition reaction.



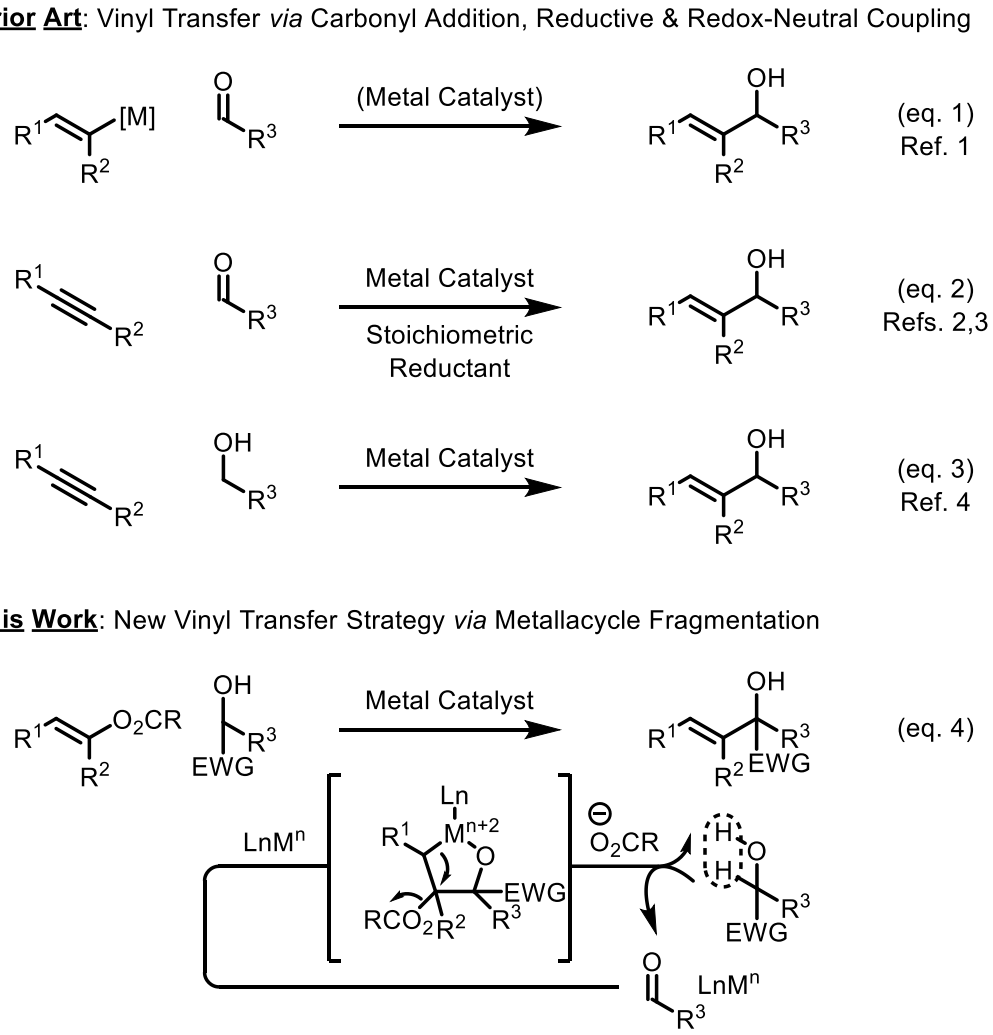
Scheme 1.64 Proposed mechanism of Ru(0) catalyzed [2+2] cycloaddition reaction.

Reactions where reductive elimination would happen after 5-membered ruthenacycle without any substrate insertion would produce 4-membered ring cycloadducts. While Ru(II) catalyzed [2+2] cycloaddition reaction was reported in good yield in 1979, $Ru_3(CO)_{12}$ catalyst was not so effective because of the poor reactivity (~10%).[70] In 1987, the Mitsudo group found that Ru(cod)(cot) complex showed much higher reactivity than $Ru_3(CO)_{12}$ (Scheme 1.63).[71] The reaction of acetylenedicarboxylate and norbornene with Ru(cod)(cot) catalyst and PBu_3 ligand at

100 ˚C gave the corresponding cyclobutene derivative in quantitative yield. This reaction only works with norbornene or norbornene derivatives. The mechanism is shown in scheme 1.64. The reaction begins with ruthenium coordination to norbornene and alkyne. Cyclometallation and successive reductive elimination furnish the [2+2] cycloadduct.

Chapter 2: Vinyl Transfer from Enol Carboxylates to Secondary Alcohol C-H Bonds *via* Metallacycle Fragmentation: Osmium Catalyzed C-C Bond Forming Transfer Hydrogenation*

2.1 Introduction



Scheme 2.1. Convergent Methods for the Synthesis of Allylic Alcohols through Vinyl Transfer.

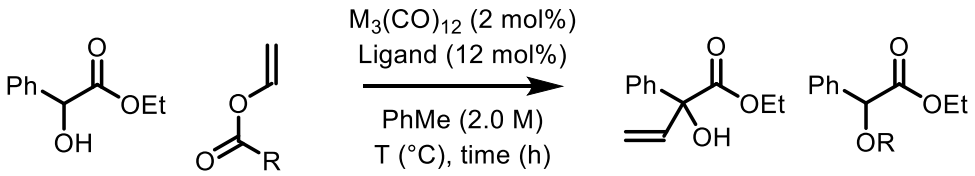
*This chapter is based on the published work:
Park, B. Y.; Luong, T.; Sato, H.; Krische, M. J. *J. Am. Chem. Soc.* **2015**, *137*, 7652.
Contribution of HS: Half of the ethylmanderate scope and half of diol scope, and preparation of a few enol carboxylates were done by HS.

Carbonyl vinylation is a powerful method for the synthesis of allylic alcohols, which are seen in many natural products and biologically important molecules. While these reactions usually require stoichiometric amount of vinylmetal reagents (Scheme 2.1, eq. 1),[1] metal catalyzed alkyne-carbonyl reductive coupling reactions[2,3] bypass discrete use of organometallic reagents. However, except hydrogen-mediated processes,[3] stoichiometric metallic, pyrophoric, or mass-intensive reductants are often required (Scheme 2.1, eq. 2).[2] More recently, ruthenium[4a,b] or nickel catalyzed redox-neutral alcohol-alkyne vinylations have been reported (Scheme 2.1, eq. 3).[4c] Still, these reactions have limitation on the scopes as the reductive coupling of acetylene and terminal alkynes to access terminal alkenes was ineffective.[5] Herein, we report a new strategy to synthesize vinyl alcohol for catalytic vinyl transfer from enol carboxylates to activated ketones through oxidative coupling-metallacycle fragmentation pathways (Scheme 2.1, eq. 4). This method enables formal direct vinylation of secondary alcohol C-H bonds in vicinally deoxygenated systems (e.g. α-hydroxy esters, 1,2-diols), including the introduction of terminal alkenes.

2.2 Reaction Development and Scope

Initial experiment with mandelate **2.1a** and **2.2a** was inspired by established conditions for ruthenium(0) catalyzed C-C couplings of activated secondary alcohols with 1,3-dienes,[6] and earlier studies on the ruthenium(0) catalyzed Pauson-Khand reaction of vicinal dicarbonyl compounds.[7] Control experiments in the absence of the precatalyst components revealed small quantities of acyl transfer to form *O*-Ac-**2.1a** (Table 2.1, entries 1 and 2). To our delight, in the presence of XPhos ligand, ethyl mandelate **2.1a** and vinyl acetate **2.2a** reacted to form a 1:1 mixture of the desired vinyl transfer product **2.3a** and *O*-Ac-**2.1a** in a combined 29% yield (Table 2.1, entry 3). The use

Table 2.1 Selected Optimization Experiments in the Redox-Triggered C-H Vinylation of Ethyl Mandelate **2.1a**.[a]



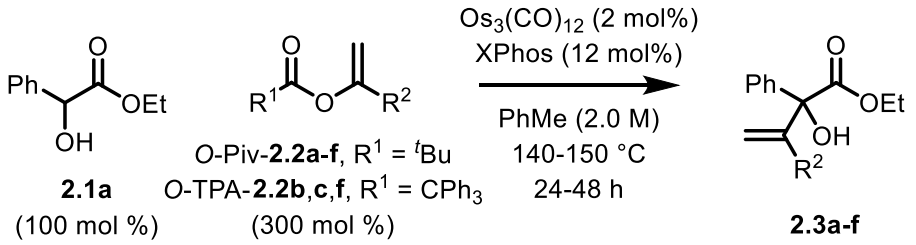
2.1a (100 mol %) | *O*-Ac-**2.2a**, R = Me; *O*-Piv-**2.2a**, R = ^{t}Bu | **2.3a** | *O*-Ac-**2.1a**, R = Ac; *O*-Piv-**2.1a**, R = Piv

Entry	**2.2a** (mol%)	M	Ligand	T (°C)	time (h)	**3a**:*O*-Ac/Piv-**1a**
1	*O*-Ac-**2.2a** (500)	-	-	130	20	trace (0:1)
2	*O*-Ac-**2.2a** (500)	-	XPhos	130	20	trace (0:1)
3	*O*-Ac-**2.2a** (500)	Ru	XPhos	130	20	29 (1:1)
4	*O*-Ac-**2.2a** (500)	Os	XPhos	130	20	85 (9.5:1)
5	*O*-Piv-**2.2a** (500)	Os	XPhos	130	24	75 (>20:1)
6	*O*-Piv-**2.2a** (500)	Os	XPhos	140	24	86 (>20:1)
⇨ **7**	*O*-Piv-**2.2a** (300)	**Os**	**XPhos**	**140**	**24**	**83** (>20:1)
8	*O*-Piv-**2.2a** (200)	Os	XPhos	140	24	76 (>20:1)
9	*O*-Piv-**2.2a** (300)	Os	RuPhos	140	24	72 (>20:1)
10	*O*-Piv-**2.2a** (300)	Os	PCy_3	140	24	50 (>20:1)
11	*O*-Piv-**2.2a** (300)	Os	PCy_2Ph	140	24	28 (>20:1)
12	*O*-Piv-**2.2a** (300)	Os	-	140	24	trace (>20:1)

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details

of $Os_3(CO)_{12}$ instead of $Ru_3(CO)_{12}$ under otherwise identical conditions dramatically improved the yield to 85% of vinyl transfer product **2.3a** and *O*-Ac-**2.1a** in a 9.5:1 ratio (Table 2.1, entry 4). The enhanced performance of osmium(0) catalyst could be attributed to the strong coordination to vinyl moiety in *O*-Ac-**2.1a** thanks to π-backbonding.[8] To avoid the undesired byproduct *O*-Ac-**2.1a** formation, the use of vinyl pivalate **2.2b** was explored (Table 2.1, entries 5 and 6). The reaction of ethyl mandelate **2.1a** with vinyl pivalate **2.2a** produced adduct **2.3a** in 75% isolated yield with complete excluded acyl transfer pathways (Table 2.1, entry 5). A modest increase in temperature improved the isolated yield of **2.3a** to 86% (Table 2.1, entry 6). Variation in the loading of **2.2a** was explored under these conditions (Table 2.1, entries 6-8), and a loading of 300 mol% was an optimal condition (Table 2.1, entry 7). Ligand screening did not increase the yield (Table 2.1,

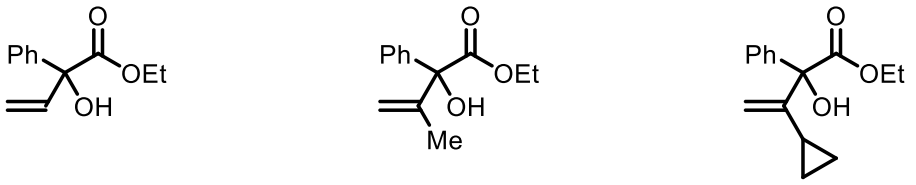
Table 2.2. Redox-Triggered C-C Coupling of Ethyl Mandelate 1a with Enol Carboxylates *O*-Piv-**2.2a**-**2.2f** or *O*-TPA-**2.2b, 2.2c, 2.2f** to Form Adducts **2.3a**-**2.3f**.



2.2a, R^2 = H
2.2d, R^2 = Ph

2.2b, R^2 = Me
2.2e, R^2 = 3,5-$(CF_3)_2$Ph

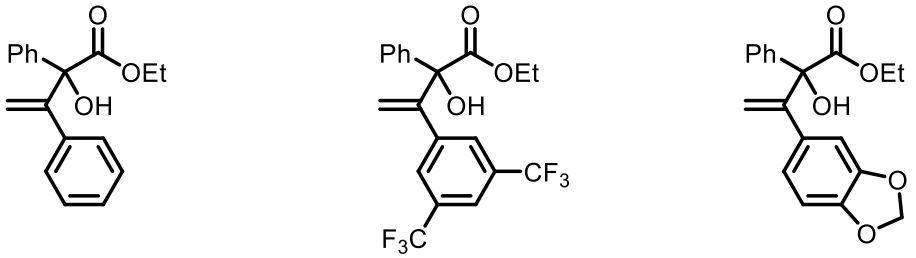
2.2c, R^2 = *c*-Pr
2.2f, R^2 = benzodioxole



2.3a, 83% Yield (*O*-Piv)

2.3b, 53% Yield (*O*-Piv)
80% Yield (*O*-TPA)

2.3c, *not formed* (*O*-Piv)
65% Yield (*O*-TPA)



2.3d, 71% Yield (*O*-Piv)

2.3e, 80% Yield (*O*-Piv)

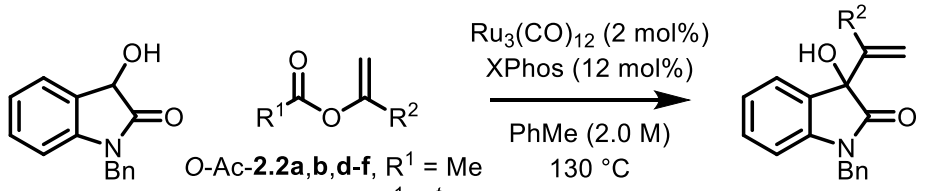
2.3f, 20% (*O*-Piv)
68% Yield (*O*-TPA)[b]

[a]Yields are of material isolated by silica gel chromatography. [b]$Os_3(CO)_{12}$ (4 mol%) and XPhos (24 mol%), isolated yield based on recovered starting material. See Supporting Information for further experimental details

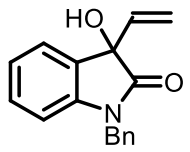
entries 9-11). In the absence of ligand, only trace amount of **2.3a** were observed (Table 2.1, entry 12). Experiments with other related vinyl donors, such as vinyl halide and vinyl ether, were ineffective.

To assess the generality of this reaction, ethyl mandelate **2.1a** was paired with various vinyl pivalates *O*-Piv-**2.2a**-**2.2f** under these optimal conditions (Table 2.2). Although the unsubstituted

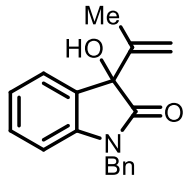
Table 2.3. Redox-Triggered C-C Coupling of 3-Hydroxy Oxindole **2.1b** with Enol Carboxylates O-Ac-**2.2a**-**2.2f** or O-Piv-**2.2c**, **2.2e**, **2.2f** to Form Adducts **2.4a**-**2.4f**.



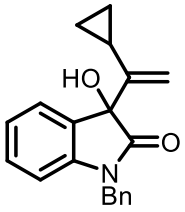
2.2a, R^2 = H | **2.2b**, R^2 = Me | **2.2c**, R^2 = *c*-Pr
2.2d, R^2 = Ph | **2.2e**, R^2 = 3,5-$(CF_3)_2$Ph | **2.2f**, R^2 = benzodioxole



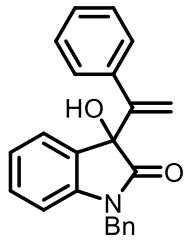
2.4a, 99% Yield (*O*-Ac)



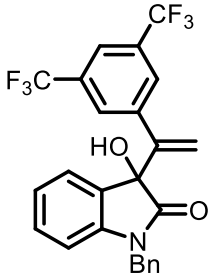
2.4b, 85% Yield (*O*-Ac)



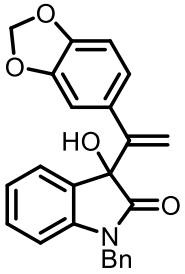
2.4c, 60% (*O*-Piv)
85% Yield (*O*-TPA)



2.4d, 87% Yield (*O*-Ac)



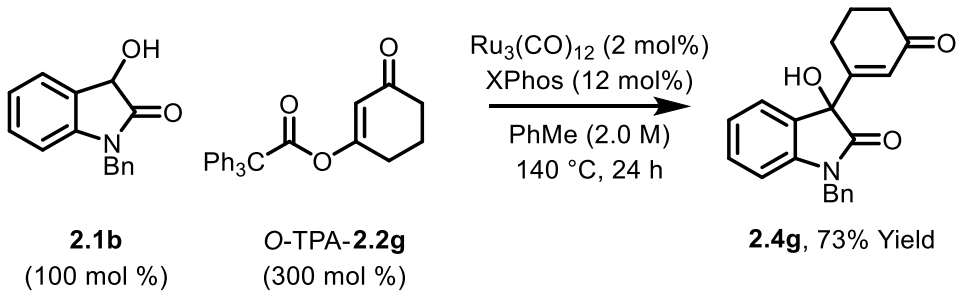
2.4e, *not formed* (*O*-Ac)
94% Yield (*O*-Piv)



2.4f, *not formed* (*O*-Ac)
90% Yield (*O*-Piv)

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

vinyl pivalate *O*-Piv-**2.2a** is an efficient partner for vinyl transfer, the use of highly substituted vinyl pivalates *O*-Piv-**2.2b-2.2f** was less efficient due to competing *O*-acylation. The use of alternative vinyl transfer substrates triphenyl acetates *O*-TPA-**2.2b**, **2.2c**, **2.2f** suppresses transesterification, delivering the desired products of vinyl transfer **2.3b**, **2.3c**, **2.3f** in moderate to excellent yields (Table 2.2). *N*-Benzyl-3-hydroxy-2-oxindole 2.1b was subjected under the optimal



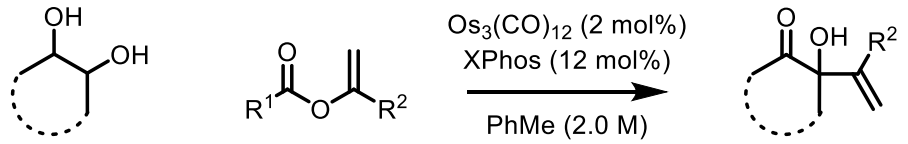
2.1b (100 mol %) | *O*-TPA-**2.2g** (300 mol %) | **2.4g**, 73% Yield

Scheme 2.2. Redox-Triggered C-C Coupling of 3-Hydroxy Oxindole **2.1b** with Enone *O*-TPA-**2.2g.**

conditions with vinyl transfer substrates (Table 2.3). Dehydrogenation of **2.1b** produces a highly reactive isatin which readily engages in oxidative coupling, suppressing competitive transesterification undesired reaction pathway. However, in certain cases the vinyl pivalates are required to control *O*-acylation and C-C coupling pathways with modified vinyl transfer substrates. The enol acetates *O*-Ac-**2.2e** and *O*-Ac-**2.2f** fail to give the desired adducts **2.4e** and **2.4f**, respectively due to acyl transfer. In contrast, the corresponding vinyl pivalates *O*-Piv-**2.2e** and *O*-Piv-**2.2f** provided adducts **2.4e** and **2.4f** in 94% and 90% yields, respectively. Finally, the transfer vinylation of conjugated enones alkene to convert 3-hydroxy-2-oxindole **2.1b** into adduct **2.4g** demonstrates the feasibility of transferring tri-substituted alkenes (Scheme 2.2).

Vicinal diols, which can form 1,2-diketones via hydrogen transfer as reactive intermediates, were also examined as electrophilic partners in vinyl transfers using *O*-Piv-**2.2a**, *O*-TPA-**2.2d** and *O*-TPA-**2.2c** (Table 2.4). As the reactions of vicinal diols **2.1c**-**2.1h** are oxidative reactions, they require excess vinyl donor as sacrificial hydrogen accepter. It was found that aryl substituted 1,2-diols **2.1c**-**2.1g** react with *O*-Piv-**2.2a** to form adducts **2.5a**-**2.5e** in moderate to good yields. For non-symmetric diols **2.1a**, **2.1b**, **2.1d** and **2.1e**, the vinyl transfer proceeds in a completely regioselective manner and can be explained on the basis of our previous density functional theory (DFT) calculation studies in related alkyne-diol C-C coupling reactions.[12] The more substituted

Table 2.4. Redox-Triggered C-C Coupling of 1,2-Diols **2.1c-2.1h** with Enol Carboxylate O-Piv-**2.2a**, O-TPA-**2.2d** and O-TPA-**2.2c** to Form Adducts **2.5a-2.5f** and **2.6a**, **2.6b**, **2.6d-2.6f**.[a]

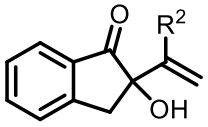


2.1c-h (100 mol %)

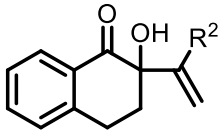
O-Piv-**2.2a**, *O*-TPA-**2.2d**, *O*-TPA-**2.2c** (500 mol %)

2.5a-e, **2.6a, 2.6b** **2.6e, 2.6f**

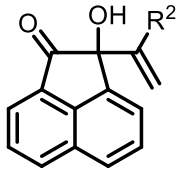
2.1c, *trans*-indane-1,2-diol **2.1d**, *trans*-tetrahydronaphthalene-1,2-diol
2.1e, *trans*-dihydroacenaphthylene-1,2-diol **2.1f**, *cis*-chroman-3,4-diol
2.1g, *cis*-2,2-dimethylchroman-3,4-diol **2.1h**, *trans*-cyclohexane-1,2-diol



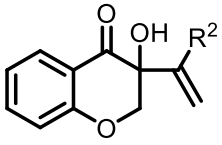
2.5a, 67% Yield
(*O*-Piv, R^2 = H)
2.6a, 71% Yield
(*O*-TPA, R^2 = *c*-Pr)



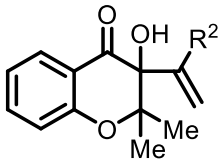
2.5b, 70% Yield
(*O*-Piv, R^2=H)
2.6b, 70% Yield
(*O*-TPA, R^2=*c*-Pr)



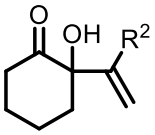
2.5c, 60% Yield
(*O*-Piv, R^2=H)
2.6c, *not formed*
(*O*-TPA, R^2=*c*-Pr)



2.5d, 88% Yield
(*O*-Piv, R^2=H)
2.6d, 93% Yield
(*O*-TPA, R^2=*c*-Pr)



2.5e, 87% Yield
(*O*-Piv, R^2=H)
2.6e, 82% Yield
(*O*-TPA, R^2=*c*-Pr)



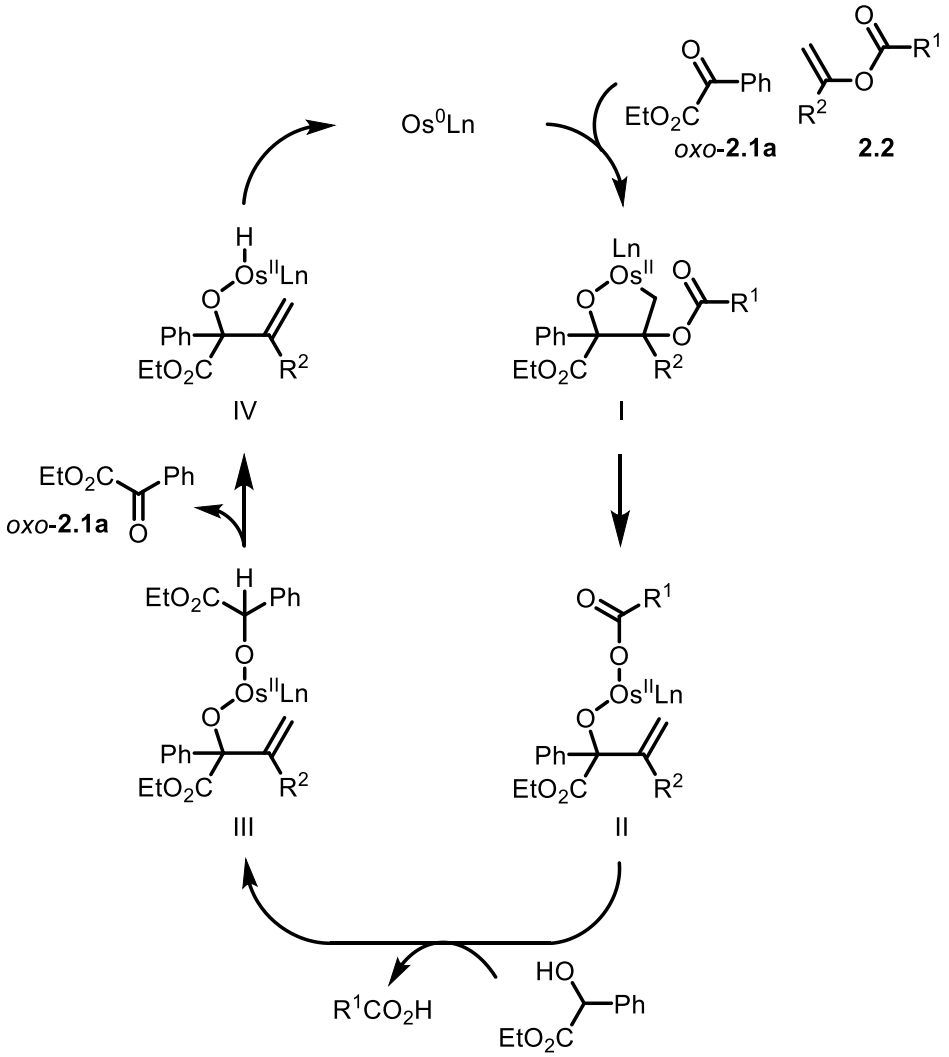
2.5f, 40% Yield
(*O*-TPA, R^2=Ph)
2.6f, 65% Yield
(*O*-TPA, R^2=*c*-Pr)

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

triphenyl acetate *O*-TPA-**2.2c** reacts with aryl substituted diols **2.1c**-**2.1g**, to furnish vinylated products **2.6a**, **2.6b**, **2.6d** and **2.6e** up to 93%. **2.6c** was not formed presumably due to steric issues. Aliphatic vicinal diols, such as cyclohexane diol 2.1h, are participated in vinyl transfer to give **2.5f** and **2.6f** in moderate yield.

2.3 Mechanism and Discussion

A proposed mechanism is illustrated for the coupling of ethyl mandelate **2.1a** with enol carboxylates **2.2** to form adducts **2.3** (Scheme 2.3). Previous mechanistic studies with $Ru_3(CO)_{12}$ precatalysts **8d** suggests the generation of mononuclear osmium(0) complex with XPhos ligand. Osmium mediated oxidative cyclometallation of *oxo*-**2.1a** with enol carboxylate **2.2** provides a β-carboxy-oxaosmacycle complex I. Related ruthenium(0) mediated carbonyl-alkene oxidative couplings are reported by Chatani and Murai[9] and our own studies.[8,12] The β-carboxy-



Scheme 2.3 Proposed general catalytic mechanism involving oxidative coupling-metallacycle fragmentation.

oxaosmacycle I undergoes fragmentation to form the osmium(II) carboxylate II,[7j,k] followed by substitution by ethyl mandelate **2.1a** resulting in osmium(II) alkoxide complex III. Successive β-hydride elimination furnishes the α-ketoester *oxo*-**2.1a** and the osmium(II) hydride IV, which upon reductive elimination provides the product 2.3.

2.4 Summary

In summary, we report a new strategy for catalytic vinyl transfer from enol carboxylates to activated secondary alcohol C−H bonds via hydrogen transfer and metallacycle fragmentation with XPhos modified ruthenium(0)- and osmium(0) catalysts. This method is applicable to activated secondary alcohols and vicinal diols **2.1a−2.1h**.

2.5 Experimental Details

I. General Information:

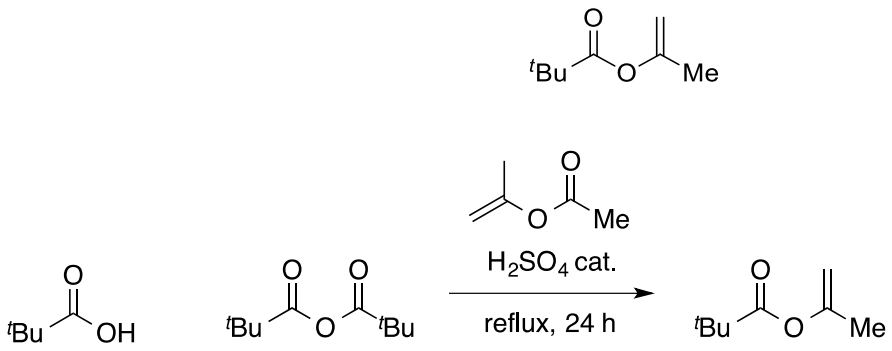
All reactions were run under an atmosphere of argon. Pressure tubes (13x100 mm) were purchased from Fischer Scientific (catalog number 14–959–35C) and were flame dried followed by cooling in a desiccator. Toluene was dried over sodium metal, benzophenone, and distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F_{254}). Visualization was accomplished with UV light followed by dipping in Seebach's stain solution then heating. Purification of reactions was carried out by flash chromatography using Silacycle silica gel (40–63 μm).

II. Spectroscopy, Spectrometry, and Data Collection:

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M+Na), or a suitable fragment ion. ^{1}H Nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in Hertz (Hz) for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.16 ppm).

Procedure for Synthesis of enol carboxylates:

Prop-1-en-2-yl pivalate (*O*-Piv-2.2b)



The procedure was similar to that reported for the preparation of other enol carboxylates.[14] To a 250 mL round-bottom flask were added pivalic acid (10 mL, 8.0 mmol), and pivalic anhydride (20 mL, 9.9 mmol). Then 50 mL of isopropenyl acetate was added followed by 2 drops of concentrated sulfuric acid. The mixture was then heated to reflux for 24 h. The mixture was allowed to cool to room temperature, and 0.5 g of sodium bicarbonate in aqueous solution was added to quench the acid catalyst. The isopropenyl acetate was then removed by evaporation under reduced pressure. The residue was purified by vacuum distillation. When the distillated compound included impurities, it was further subjected to column chromatography (2% Et_2O/pentanes) to furnish the titled compound (560 mg, 8%) as a colorless oil.

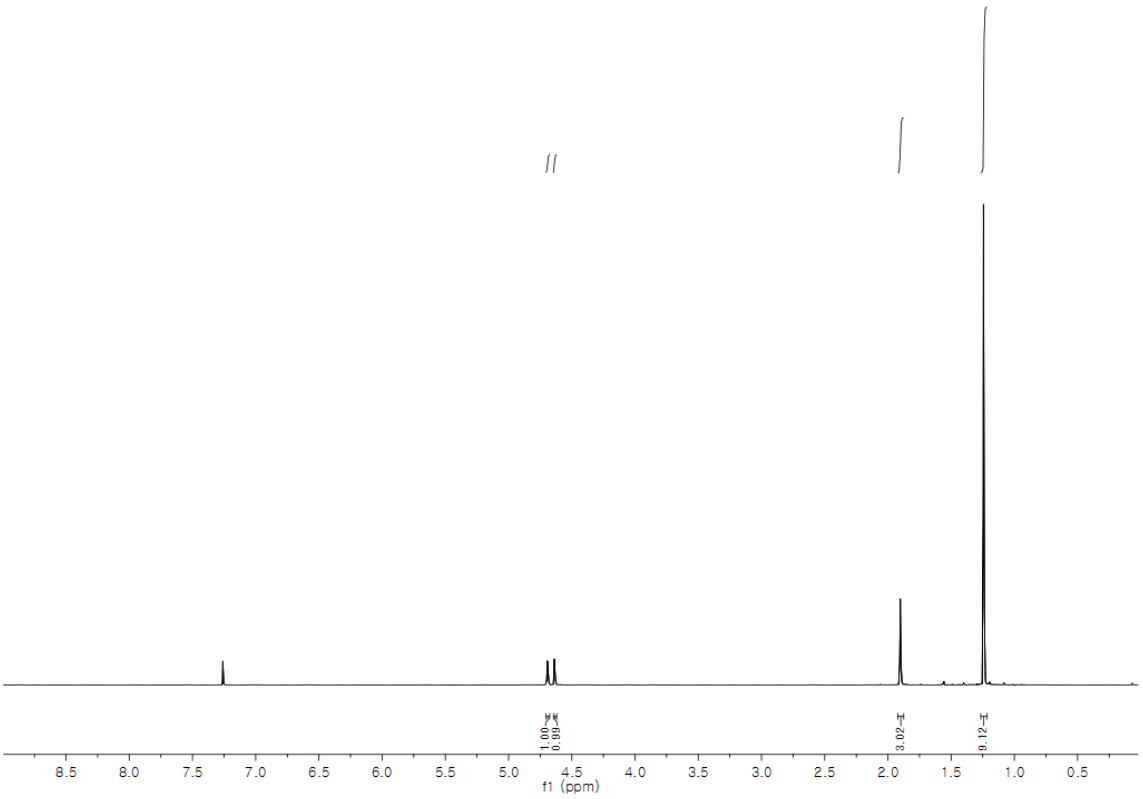
R_f: 0.48 (Hex:DCM = 3:2).

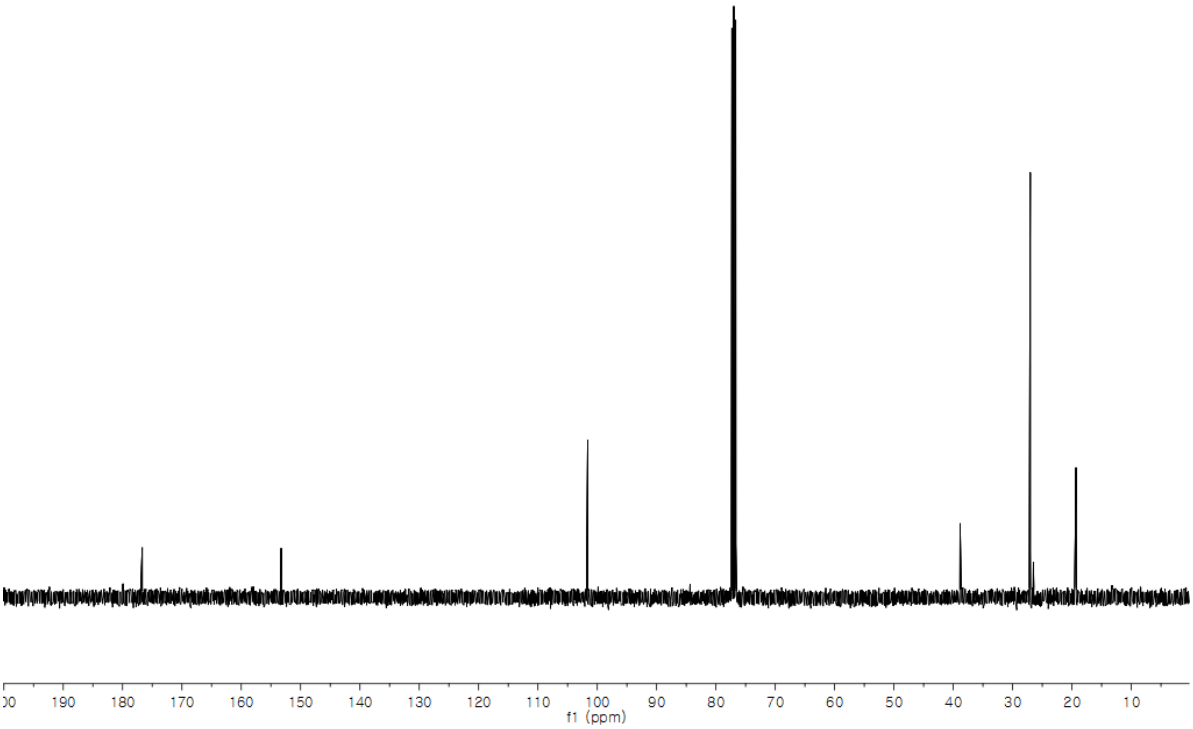
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (s, 1H), 4.64 (s, 1H), 1.90 (s, 3H), 1.24 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 153.4, 101.8, 39.0, 27.2, 19.5.

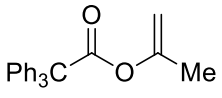
LRMS (CI) Calcd. for $C_8H_{14}O_2$ $[M+H]^+$: 143, Found: 143.

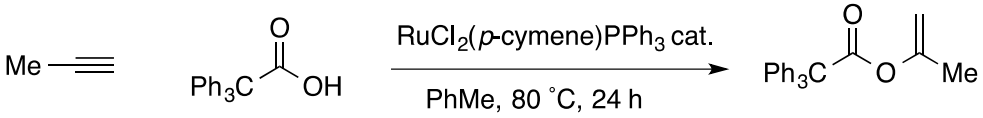
FTIR (neat): 2959, 2926, 1729.


1.00
0.99
3.02
9.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Prop-1-en-2-yl 2,2,2-triphenylacetate (*O*-TPA-2.2b)





The procedure was similar to that reported for the preparation of other enol carboxylates.[15] To a 100 mL pressure tube were added α,α-diphenylbenzeneacetic acid (2.9 g, 10 mmol) and $RuCl_2$(*p*-cymene)PPh_3 (57 mg, 0.1 mmol) in 1 M toluene. Then, condensed methyl acetylene (3.7 mL, 50 mmol) was added to the solution at -78 ˚C. The reaction mixture was stirred at 80 ˚C for 24 h. The solution was diluted with Et_2O and quenched with water. The aqueous phase was extracted with Et_2O (2 x 20 mL), then the combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography (20-30% DCM/hexanes) to furnish the title compound (1.4 g, 43%) as a white solid.

R_f: 0.45 (Hex:DCM = 3:2).

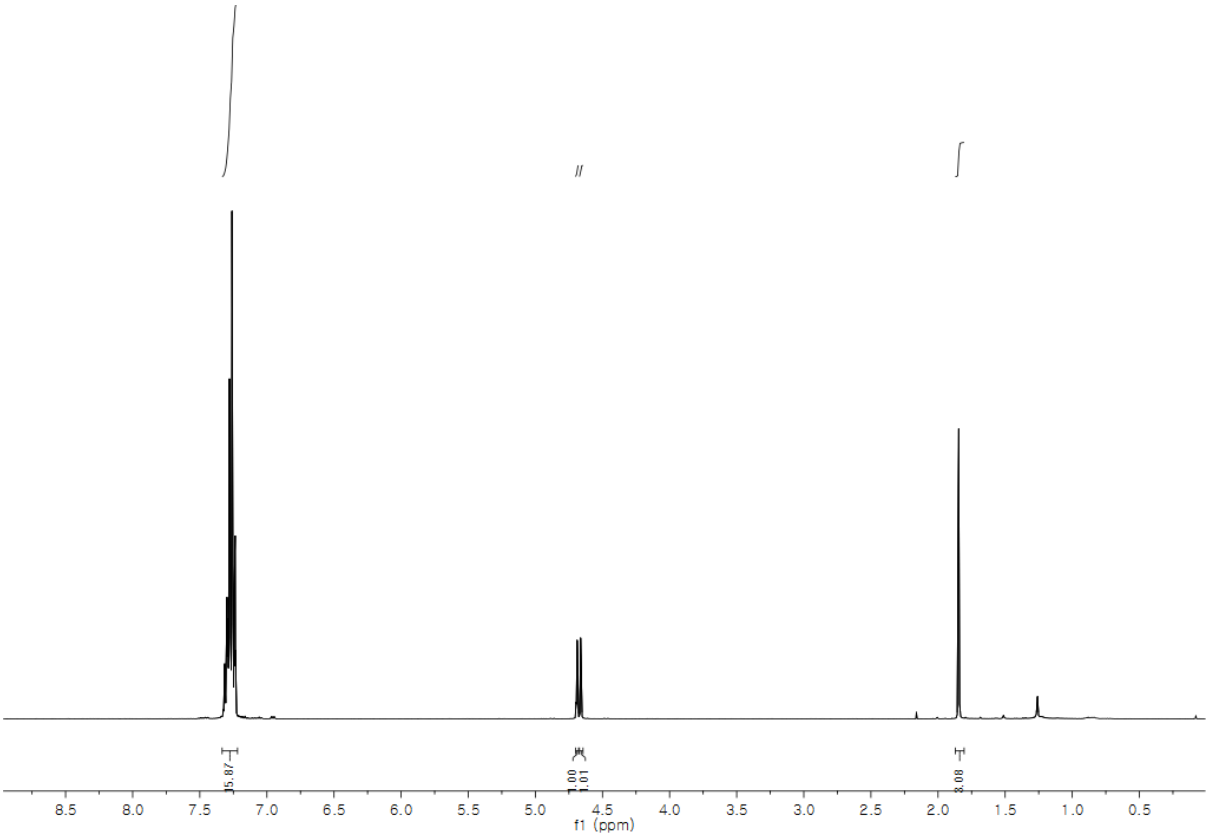
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.23 (m, 15H), 4.70-4.68 (m, 1H), 4.66 (d, *J*=1.2 Hz, 1H), 1.85 (s, 3H).

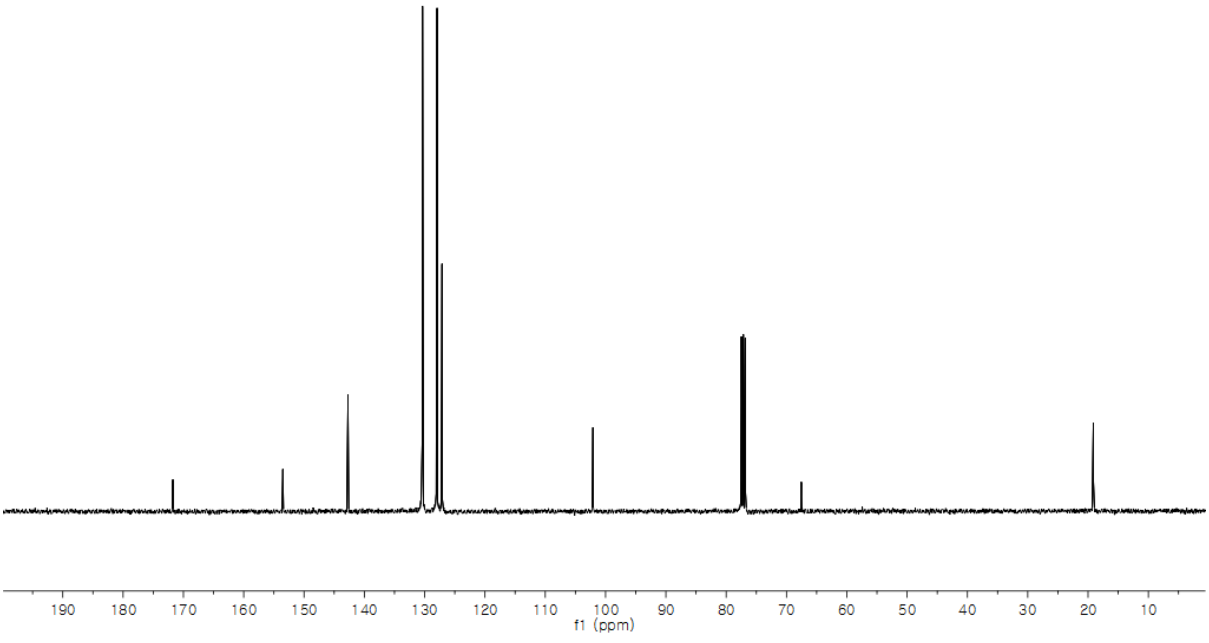
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 153.5, 142.7, 130.4, 127.9, 127.1, 102.1, 67.6, 19.1.

LRMS (CI) Calcd. for $C_{23}H_{20}O_2$ $[M+H]^+$ and $[CPh_3]$+: 329 and 243, Found: 329 and 243.

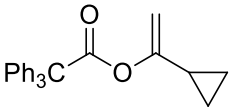
FTIR (neat): 2359, 1737.

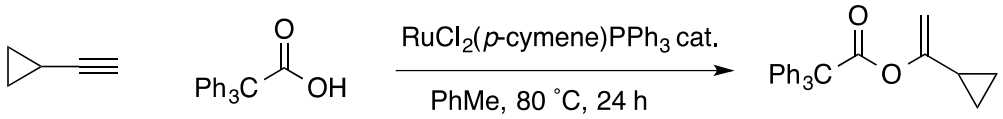
MP: 100.2–102.4 ºC


5.87
1.00
1.01
8.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Cyclopropylvinyl 2,2,2-triphenylacetate (*O*-TPA-2.2c)





The procedure was similar to that reported for the preparation of other enol carboxylates.[14] To a 100 mL round-bottom flask were added cyclopropyl acetylene (1.3 mL, 15 mmol), α,α-diphenylbenzeneacetic acid (2.9 g, 10 mmol), and $RuCl_2$(*p*-cymene)PPh_3 (57 mg, 0.1 mmol) in 1 M toluene. The reaction mixture was stirred at 80 ˚C for 24 h. The solution was diluted with Et_2O and quenched with water. The aqueous phase was extracted with Et_2O (2 x 20 mL), then the combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vaccum and the residue was subjected to column chromatography (2% AcOEt/hexanes) to furnish the title compound (2.5 g, 70%) as a white solid.

R_f: 0.45 (Hex:DCM = 3:2).

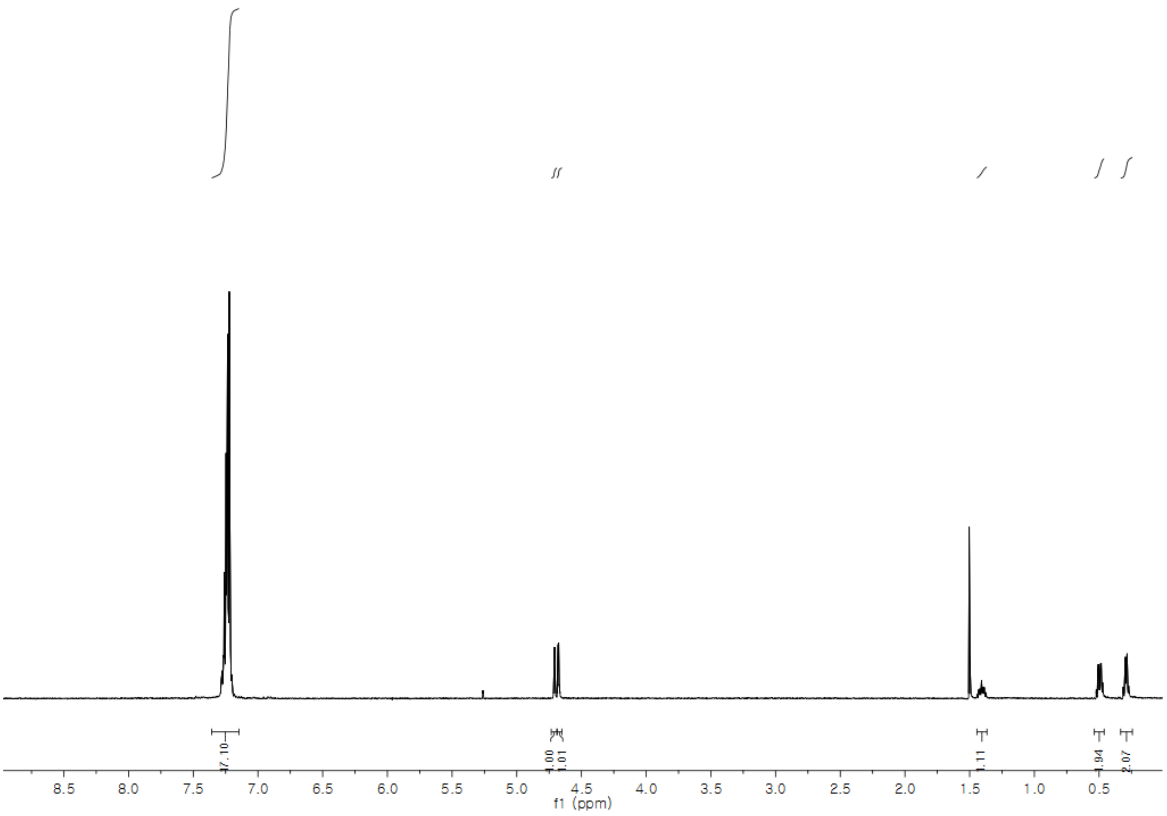
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.20 (m, 15H), 4.71 (d, *J* = 2.0 Hz, 1H), 4.68 (d, *J* = 2.0 Hz, 1H), 1.44–1.38 (m, 1H), 0.52–0.47 (m, 2H), 0.31–0.27 (m, 2H).

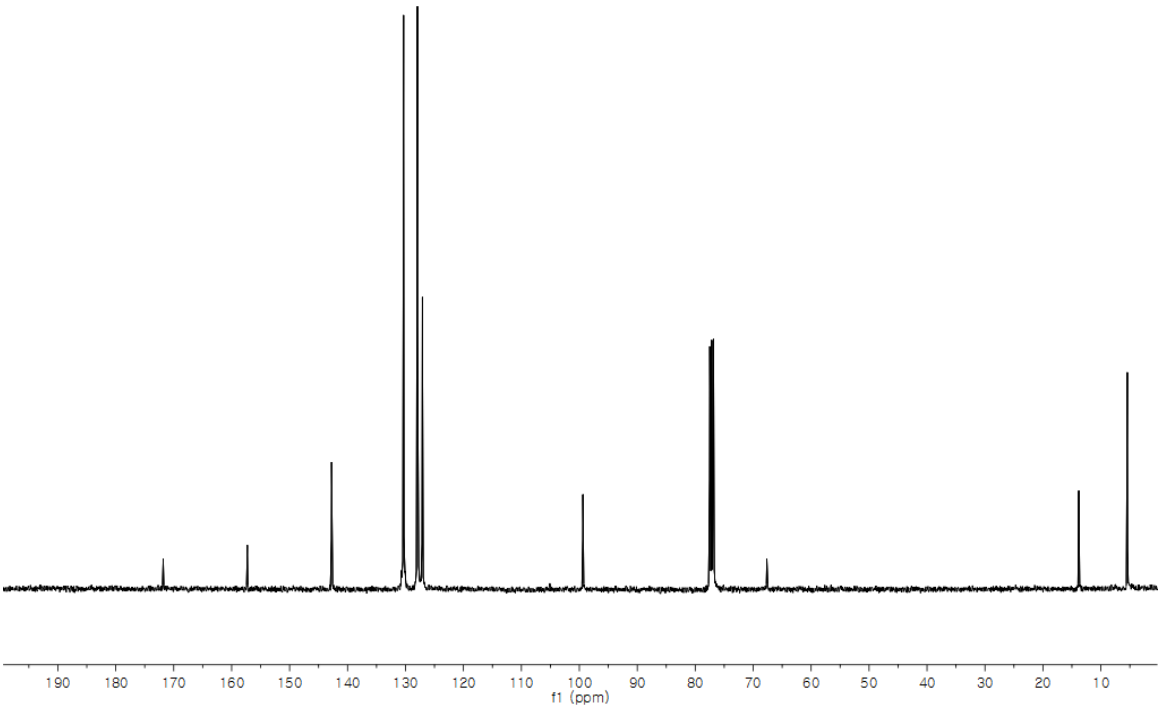
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 157.3, 142.7, 130.7, 130.3, 127.9, 127.1, 99.4, 67.6, 13.8, 5.4.

LRMS (CI) Calcd. for $C_{25}H_{22}D_2$ $[M+H]^+$ and $[CPh_3]^+$: 355 and 243, Found: 355 and 243.

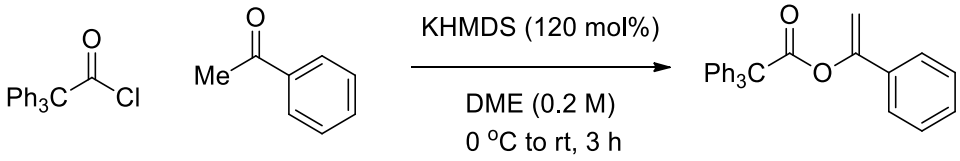
FTIR (neat): 2359, 1735, 1175.

MP: 92.8–95.6 °C


7.10
4.00
1.01
1.11
1.94
2.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Phenylvinyl 2,2,2-triphenylacetate (*O*-TPA-2.2d).



A flame-dried 50 mL round-bottom flask was charged with potassium bis(trimethylsilyl)amide (KHMDS) (1.6 g, 7.9 mmol) and DME (8 mL). To this stirring mixture aceteophenone (0.77 mL, 6.6 mmol) was added dropwise. The resulting solution was stirred for an additional 15 min and was then transferred dropwise *via* syringe to another 50 mL round-bottom flask with triphenylacetyl chloride (3.0 g, 9.8 mmol) in DME (8 mL) at 0 °C. The reaction mixture was stirred for 3 hours, and then quenched with NH_4Cl (10 mL). The solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were successively washed with water (3 × 10 mL) and brine (3 × 10 mL), and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by flash column chromatography (SiO_2, 5% EtOAc/hexanes) to afford the title compound (1.9 g, 74%) as a pale white solid.

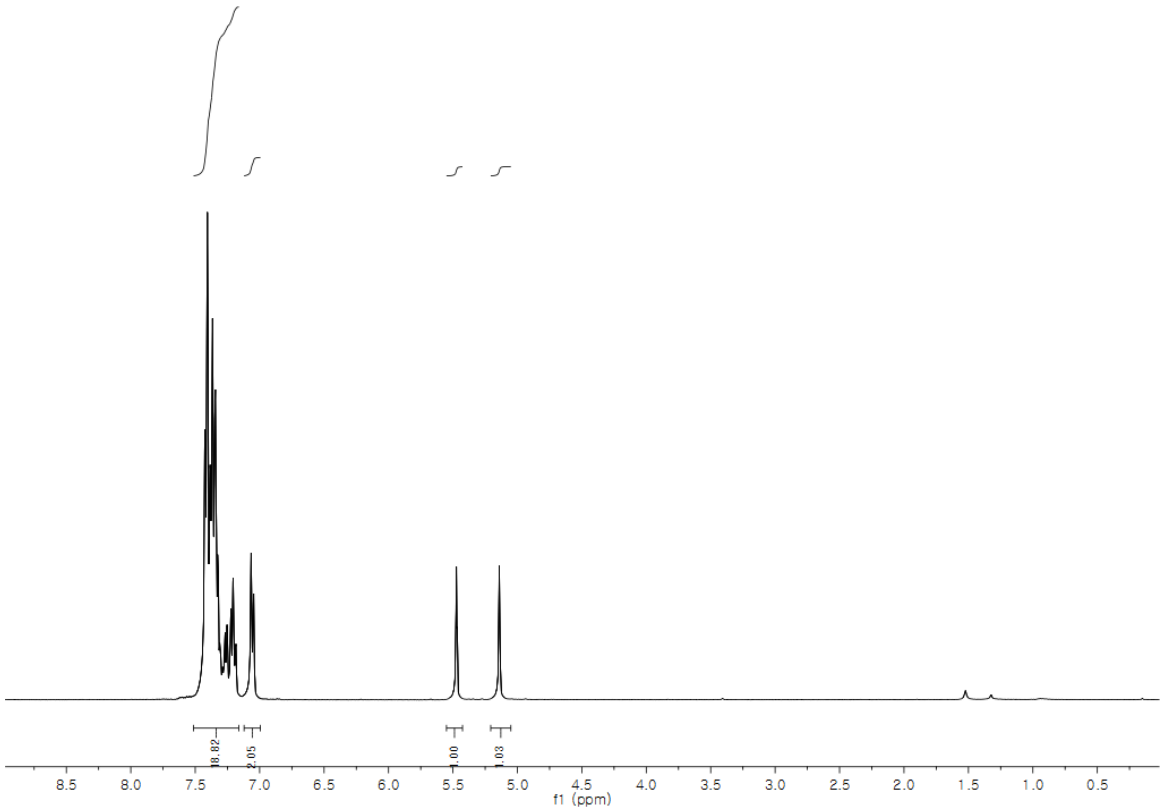
R_f: 0.60 (EtOAc:hexanes = 1:4).

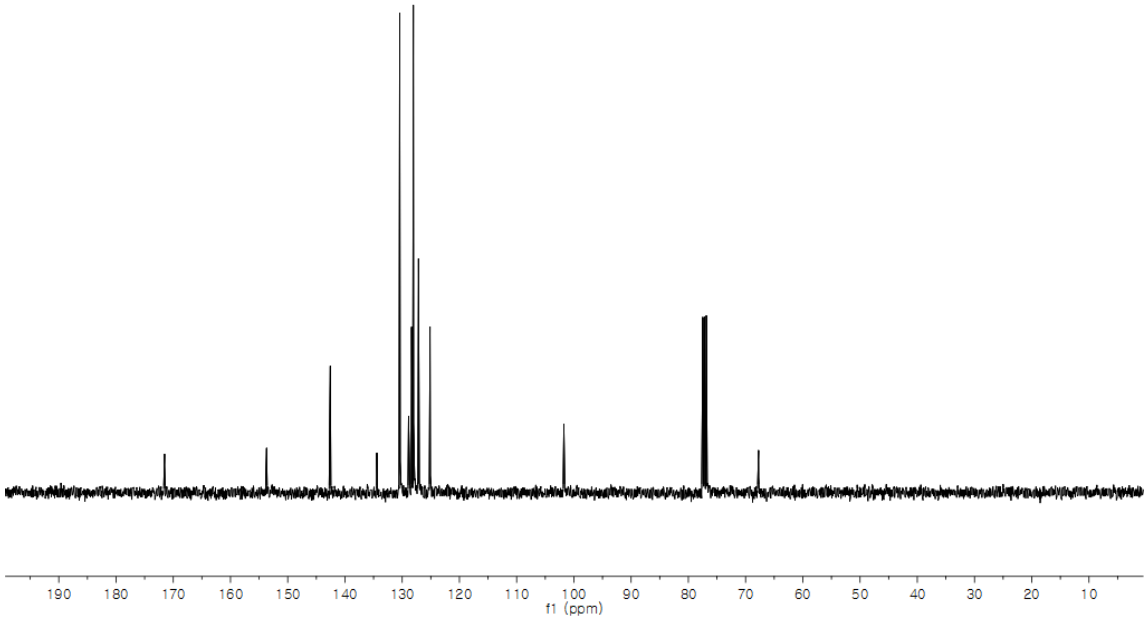
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.16 (m, 18H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.47 (dd, *J* = 2.4 Hz, 2.4 Hz, 1H), 5.14 (dd, *J* = 2.3 Hz, 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 153.7, 142.6, 134.4, 130.4, 128.9, 128.4, 128.1, 127.1, 125.1, 101.7, 67.7.

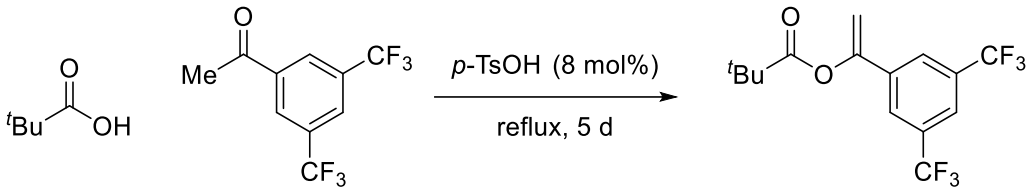
LRMS (CI) Calcd. for $C_{28}H_{22}O_2$ $[M+H]^+$: 391, Found: 391.

FTIR (neat): 3060, 1747.


18.82
2.05
1.00
1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-(3,5-Bis(trifluoromethyl)phenyl)vinyl pivalate (*O*-Piv-2.2e).



In modification to literature procedure,[16] a flame-dried 250 mL round-bottom flask was charged with 1-(3,5-bis(trifluoromethyl)-phenyl)ethan-1-one (15.4 mL, 95 mmol), vinyl dimethylpropionate (32 mL, 210 mmol) and *p*-toluenesulfonic acid (1.5 g, 7.8 mmol). The solution was refluxed for 5 days in 250 mL round-bottom flask. The mixture was allowed to cool to room temperature, and the mixture was concentrated. Ether was added (50 mL), and the resulting solvent was washed with water (3 x 20 mL) and dried over $MgSO_4$. The residue was purified by vacuum distillation. When the distillated compound included impurities, it was further subjected to flash column chromatography (SiO_2, 5% DCM/hexanes) to furnish the titled compound (2.3 g, 7%) as a white solid.

R_f: 0.60 (hexanes:DCM = 3:2).

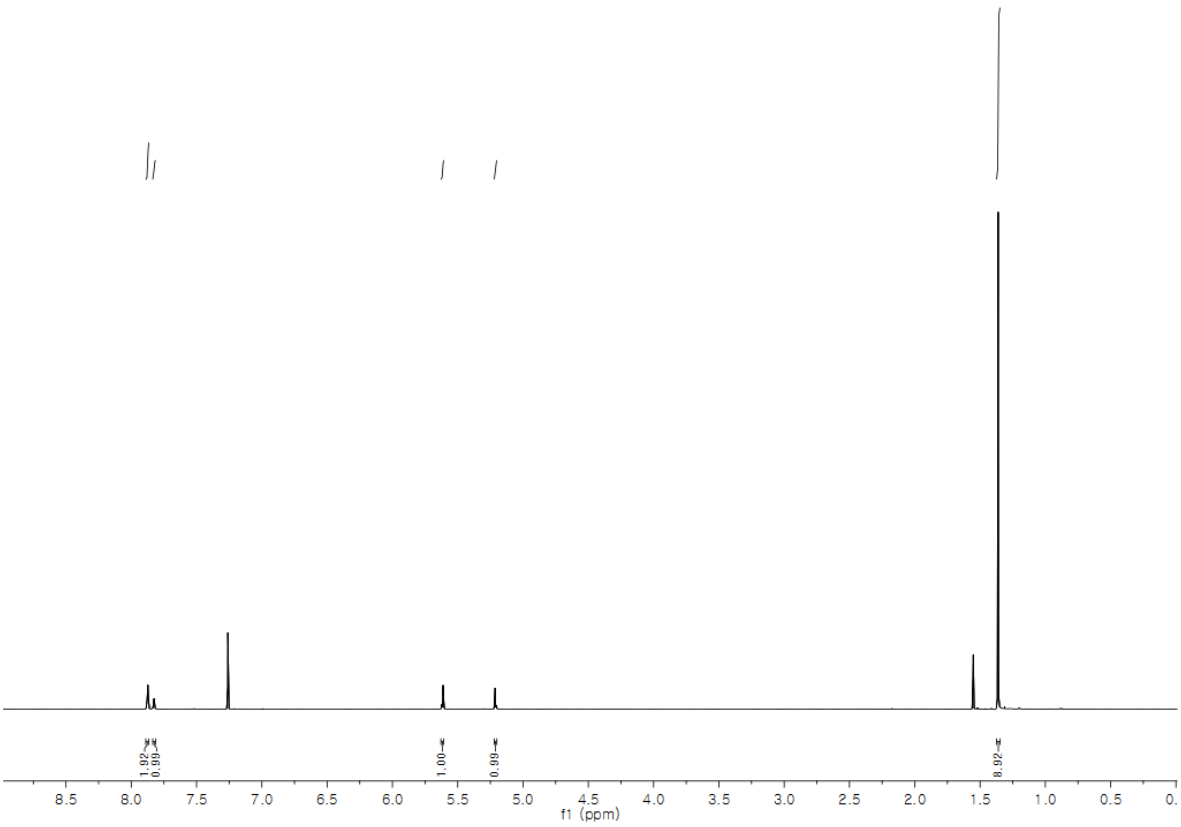
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 2H), 7.83 (s, 1H), 5.61 (d, *J* = 2.6 Hz, 1H), 5.21 (d, *J* = 2.6 Hz, 1H), 1.36 (s, 9H).

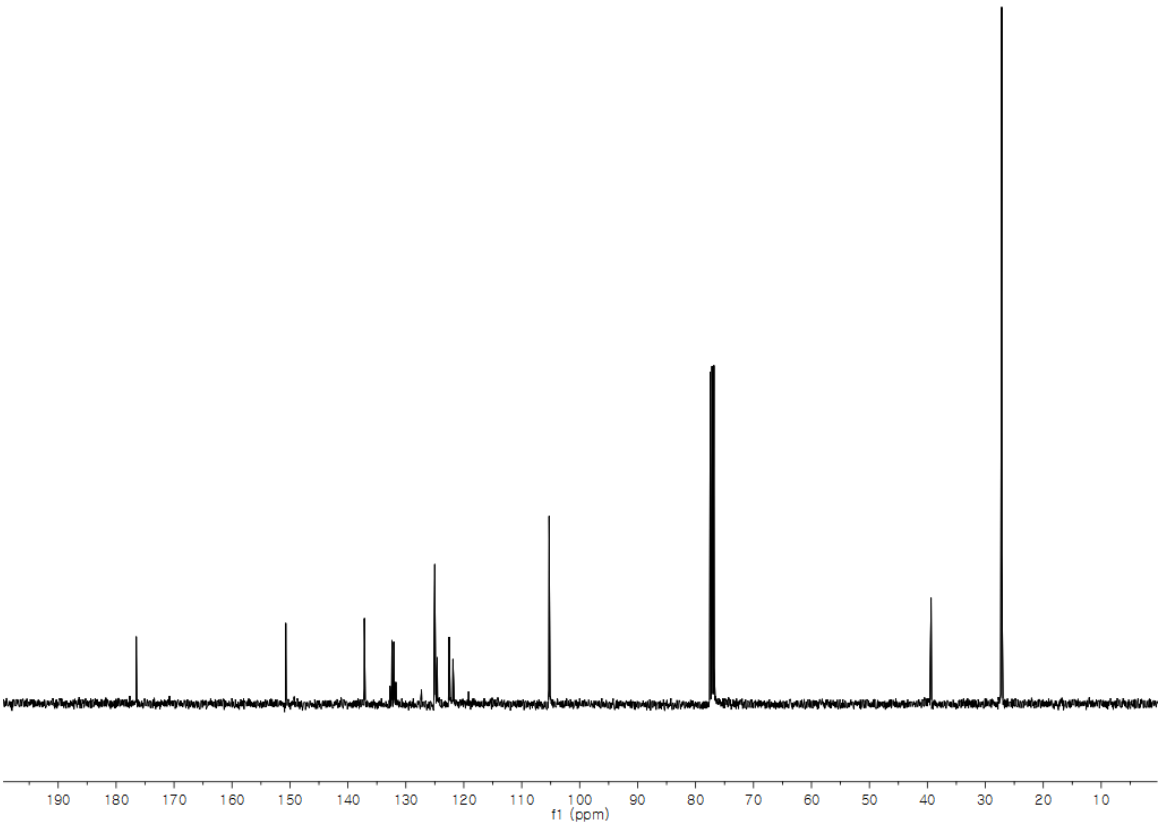
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 150.7, 137.2, 132.2 (quartet, *J* = 33.0 Hz), 125.0, 123.2 (quartet, *J* = 271.0 Hz), 122.52, 122.49, 105.3, 39.4, 27.2.

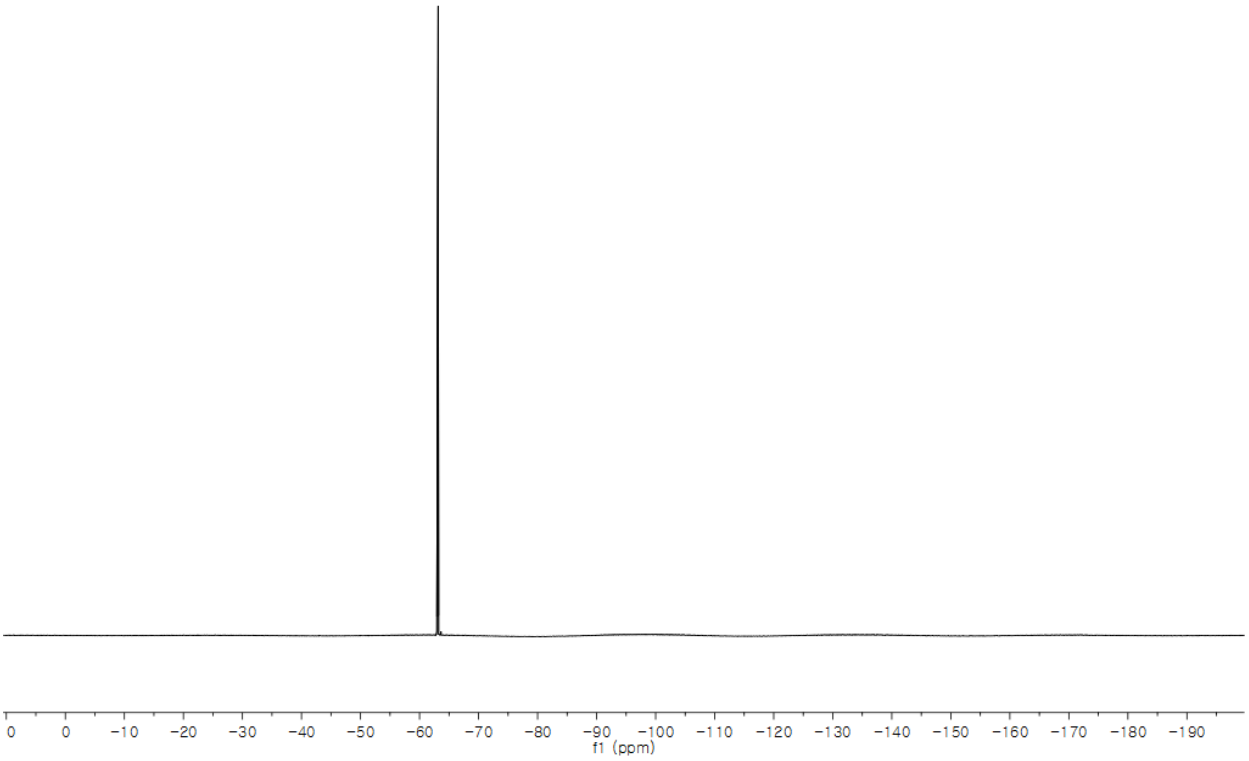
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.2.

LRMS (CI) Calcd. for $C_{15}H_{14}F_6O_2$ $[M-F]^+$: 321, Found: 321.

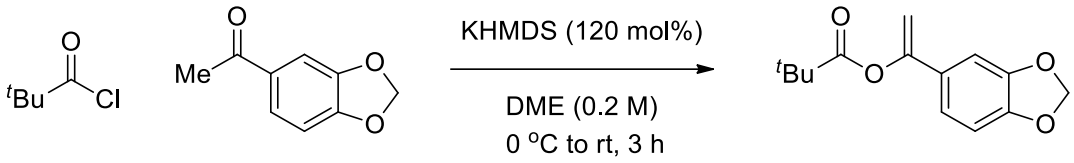
FTIR (neat): 2360, 1744. **MP**: 88.3–89.5 ºC.


1.92
0.99
1.00
0.99
8.92
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


0
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

1-(Benzo[*d*][1,3]dioxol-5-yl)vinyl pivalate (*O*-Piv-2.2f).



A flame-dried 50 mL round-bottom flask was charged with potassium bis(trimethylsilyl)amide (KHMDS) (2.4 g, 12 mmol) and DME (10 mL). To this stirring mixture 3',4'-(methylenedioxy)acetophenone (1.6 g, 10 mmol) was added dropwise. The resulting solution was stirred for an additional 15 min and was then transferred dropwise *via* syringe to another 50 mL round-bottom flask with pivaloyl chloride (1.2 mL, 10.0 mmol) in DME (10 mL) at 0 °C. The reaction mixture was stirred for 3 hours, and then quenched with NH_4Cl (10 mL). The solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were successively washed with water (3 × 10 mL) and brine (3 × 10 mL), and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by flash column chromatography (SiO_2, 5% EtOAc/hexane) to afford the title compound (0.87 g, 35%) as a white solid.

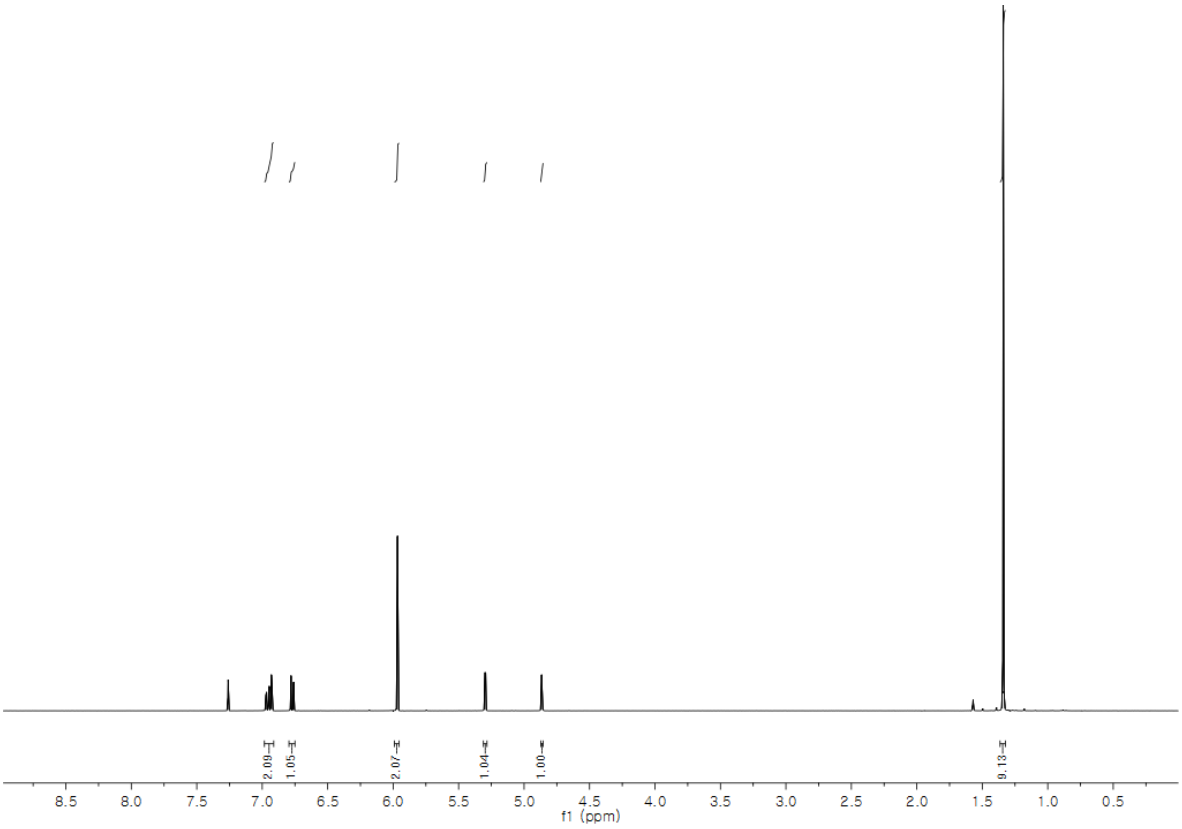
R_f: 0.27 (hexanes:DCM = 3:2).

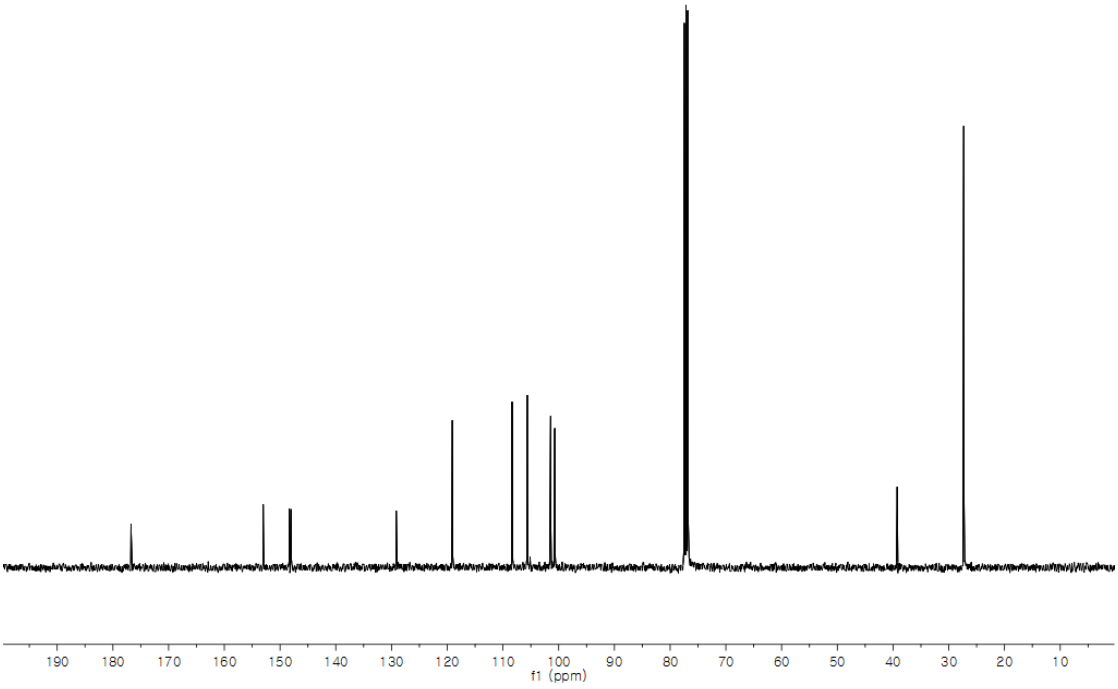
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95–6.93 (m, 2H), 6.77 (dd, *J* = 8.0 Hz, 0.4 Hz, 1H), 5.97 (s, 2H), 5.30 (d, *J* = 2.4 Hz, 1H), 4.86 (d, *J* = 2.4 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 153.0, 148.3, 148.0, 129.2, 119.1, 108.4, 105.7, 101.4, 100.7, 39.3, 27.3.

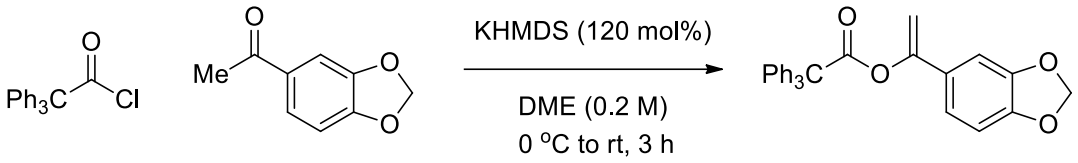
LRMS (CI) Calcd. for $C_{14}H_{16}O_4$ $[M]^+$: 248, Found: 248.

FTIR (neat): 2979, 1746. **MP**: 54.8–56.4 °C.


2.09
1.05
2.07
1.04
1.00
9.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-(Benzo[*d*][1,3]dioxol-5-yl)vinyl 2,2,2-triphenylacetate (*O*-TPA-2.2f).



A flame-dried 50 mL round-bottom flask was charged with potassium bis(trimethylsilyl)amide (KHMDS) (2.4 g, 12 mmol) and DME (10 mL). To this stirring mixture 3',4'-(methylenedioxy)acetophenone (1.6 g, 10 mmol) was added dropwise. The resulting solution was stirred for an additional 15 min and was then transferred dropwise *via* syringe to another 50 mL round-bottom flask with triphenylacetyl chloride (3.0 g, 9.8 mmol) in DME (10 mL) at 0 °C. The reaction mixture was stirred for 3 hours, and then quenched with NH_4Cl (10 mL). The solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were successively washed with water (3 × 10 mL) and brine (3 × 10 mL), and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by flash column chromatography (SiO_2, 5% EtOAc/hexanes) to afford the title compound (1.3 g, 30%) as a white solid.

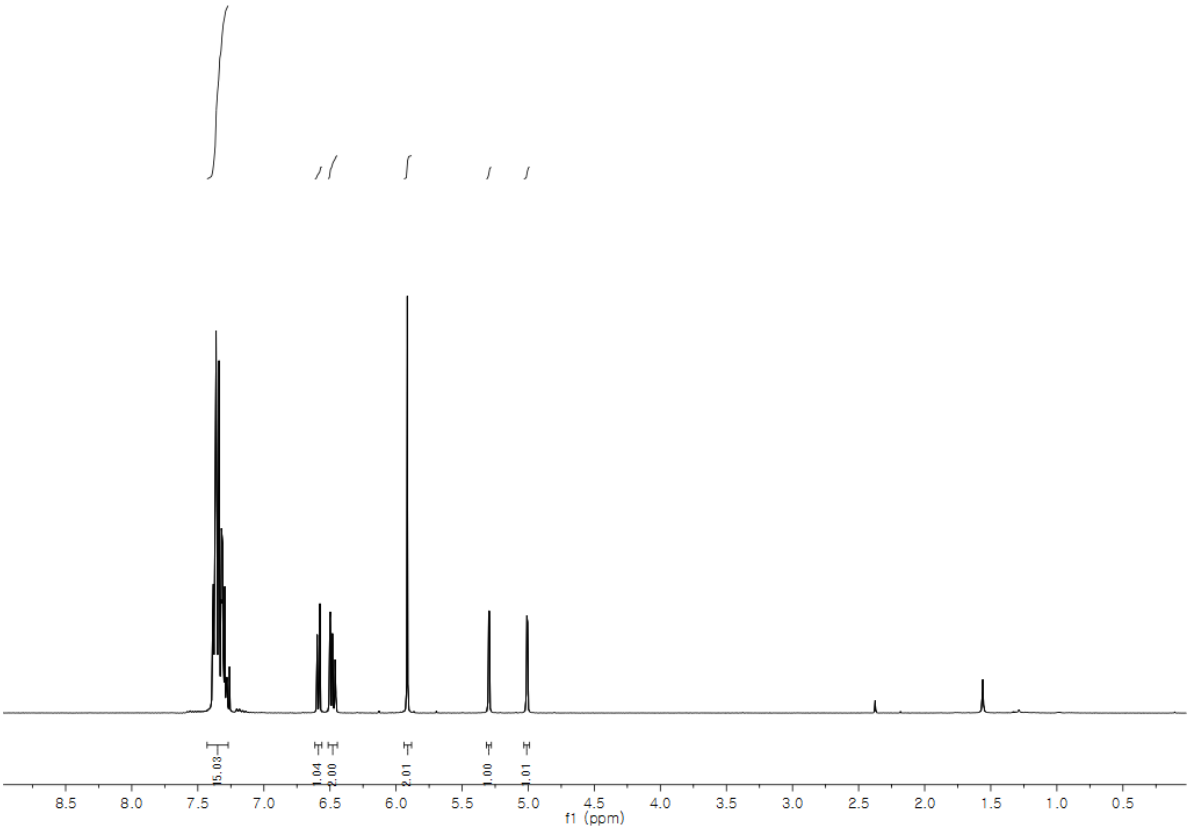
R_f: 0.27 (hexanes:DCM = 3:2).

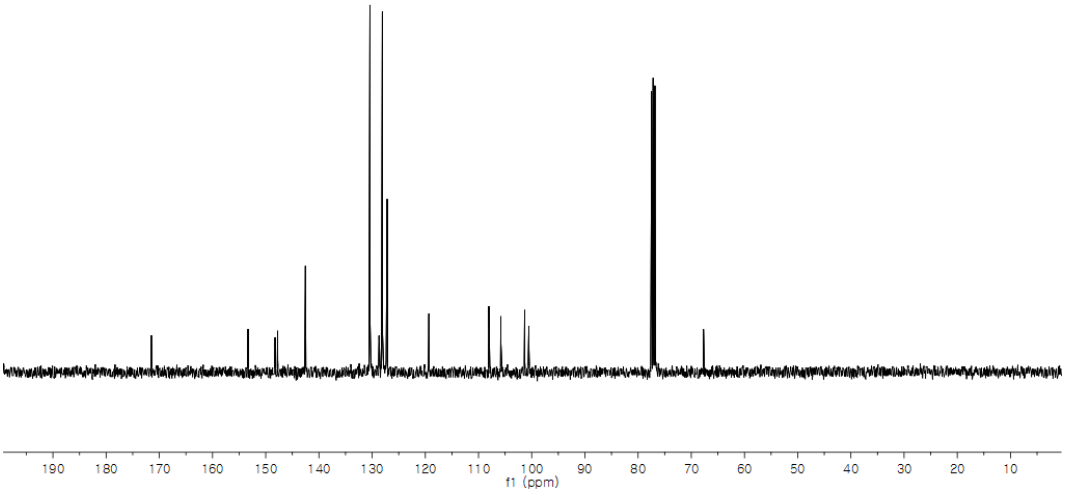
^{1}H NMR (400 MHz, $CDCl_3$): 7.43–7.27 (m, 15H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.51–6.44 (m, 2H), 5.91 (s, 2H), 5.30 (d, *J* = 2.3 Hz, 1H), 5.01 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 153.3, 148.2, 147.8, 142.5, 130.4, 128.7, 128.1, 127.2, 119.3, 108.1, 105.8, 101.3, 100.5, 67.7.

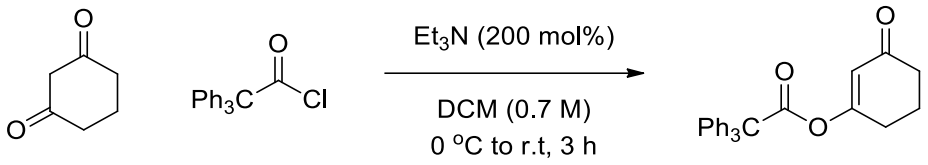
LRMS (ESI) Calcd. for $C_{29}H_{22}O_4$ $[M+Na]^+$: 457, Found: 457.

FTIR (neat): 2970, 2360, 1741.


15.03
1.04
2.00
2.01
1.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3-Oxocyclohex-1-en-1-yl 2,2,2-triphenylacetate (*O*-TPA-2.2g).



A flame-dried 25 mL round-bottom flask was charged with 1,3-cyclohexanedione (305 mg, 2.7 mmol), trimethylamine (0.76 mL, 5.4 mmol) and DCM (4 mL). To this stirring mixture 2,2,2-triphenylacetyl chloride (900 mg, 2.9 mmol) was added at 0 °C. The resulting solution was stirred for an additional 3 hours at r.t, and then quenched with water (5 mL). The solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were successively washed with water (3 × 10 mL) and brine (3 × 10 mL), and dried over Na_2SO_4. After evaporation of solvents, the residue was purified by flash column chromatography (SiO_2, 20% EtOAc/hexanes) to afford the title compound (855 mg, 82%) as a white solid.

R_f: 0.22 (EtOAc:hexanes = 1:4).

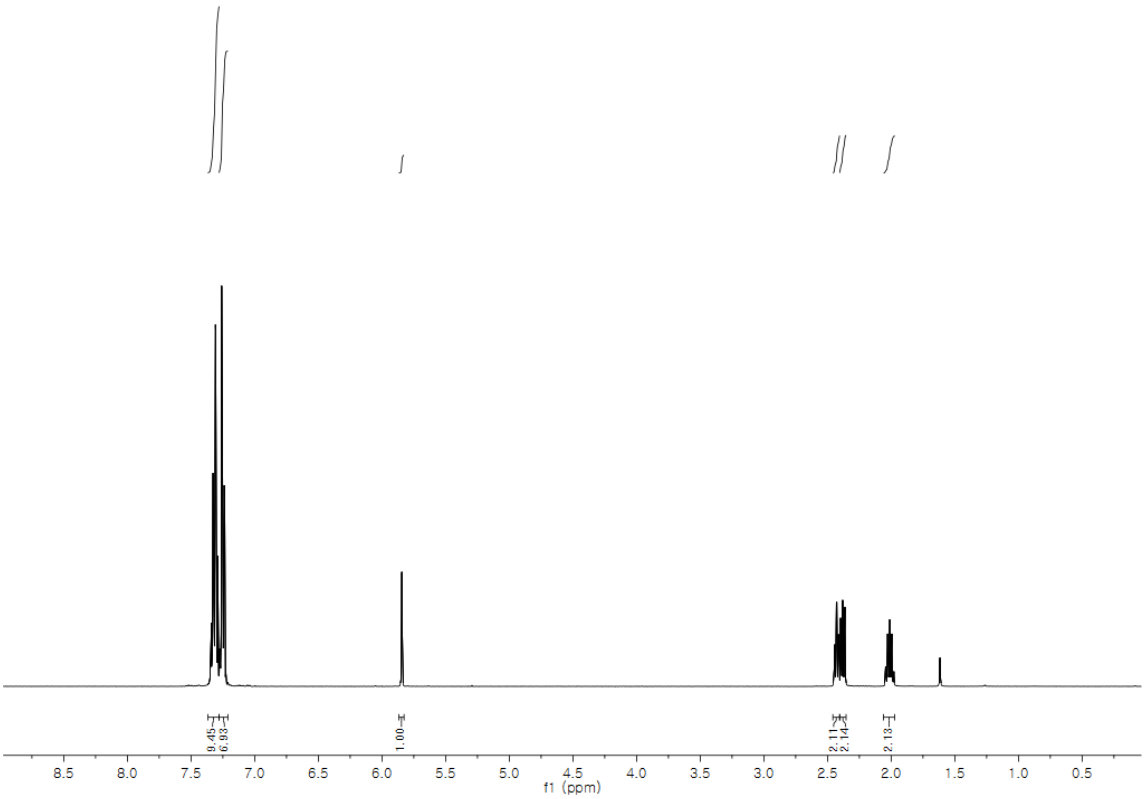
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.23 (m, 15H), 5.84 (t, *J* = 1.2 Hz, 1H), 2.43 (td, *J* = 6.2 Hz, 1.2 Hz, 2H), 2.40–2.36 (m, 2H), 2.04–1.98 (m, 2H).

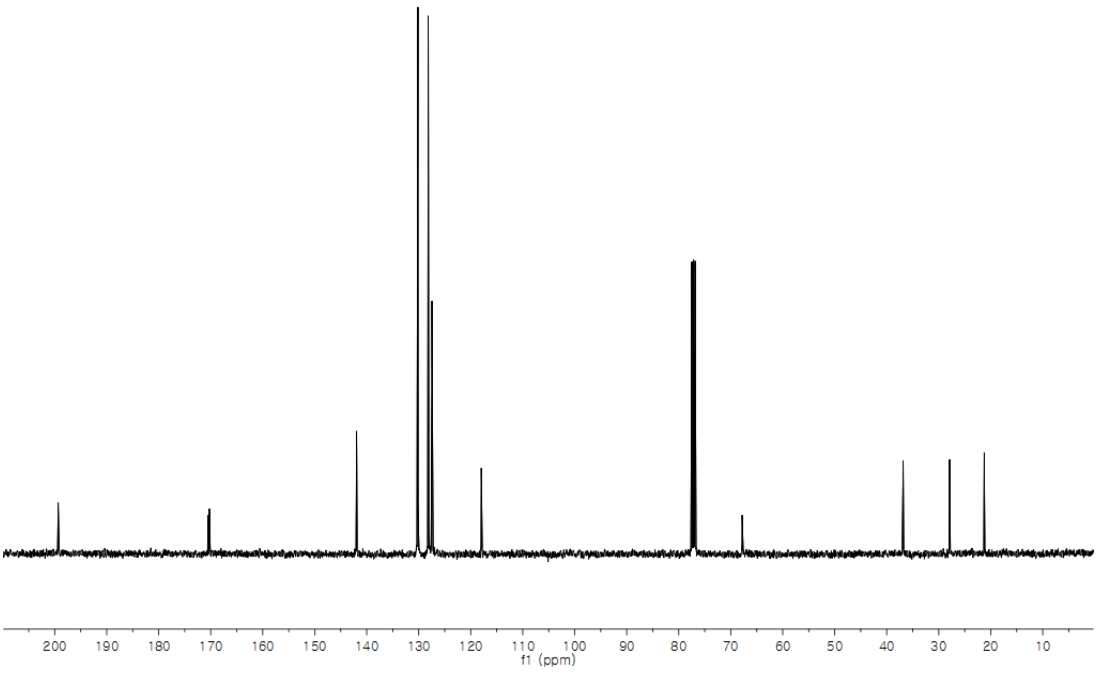
^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 170.5, 170.3, 141.9, 130.2, 128.2, 127.4, 118.0, 67.8, 36.8, 27.9, 21.3.

LRMS (ESI) Calcd. for $C_{26}H_{22}O_3$ $[M+Na]^+$: 405, Found: 405.

FTIR (neat): 3052, 1746, 1675.

MP: 159.6-160.2 °C.


9.45
6.93
1.00
2.11
2.14
2.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

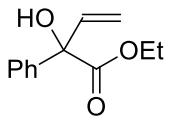

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

A. **General Procedure for Carbinol C-H Activation:**

(For solid alcohol coupling partners): A resealable pressure tube (ca. 13 x 100) was charged with M_3CO_{12} (3.9 mg of Ru_3CO_{12} or 5.5 mg of Os_3CO_{12}, 0.006 mmol, 2 mol%), XPhos (17.7 mg, 0.036 mmol, 12 mol%), and the reactant alcohol (0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. Toluene (0.15 mL, 2.0 M with respect to the alcohol reactant) was added. The enol carboxylate (0.90 mmol, 300 mol%) was added *via* syringe and the rubber septum was quickly replaced with a screw cap. The mixture was heated at the temperature stated for the time stated. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product.

(For liquid alcohol coupling partners): A resealable pressure tube (ca. 13 x 100) was charged with M_3CO_{12} (3.9 mg of Ru_3CO_{12} or 5.5 mg of Os_3CO_{12}, 0.006 mmol, 2 mol%), XPhos (17.7 mg, 0.036 mmol, 12 mol%), and the reactant alcohol (0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. Toluene (0.15 mL, 2.0 M with respect to the alcohol reactant) was added. The reactant alcohol (0.30 mmol, 100 mol%) and the enol carboxylate (0.90 mmol, 300 mol%) was added *via* syringe and the rubber septum was quickly replaced with a screw cap. The mixture was heated at the temperature stated for the time stated. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product.

Ethyl 2-hydroxy-2-phenylbut-3-enoate (2.3a).



The reaction was conducted at 140 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 2% EtOAc/hexanes to 4% EtOAc/hexanes) provided the title compound (51.4 mg, 83%) as a pale yellow oil.

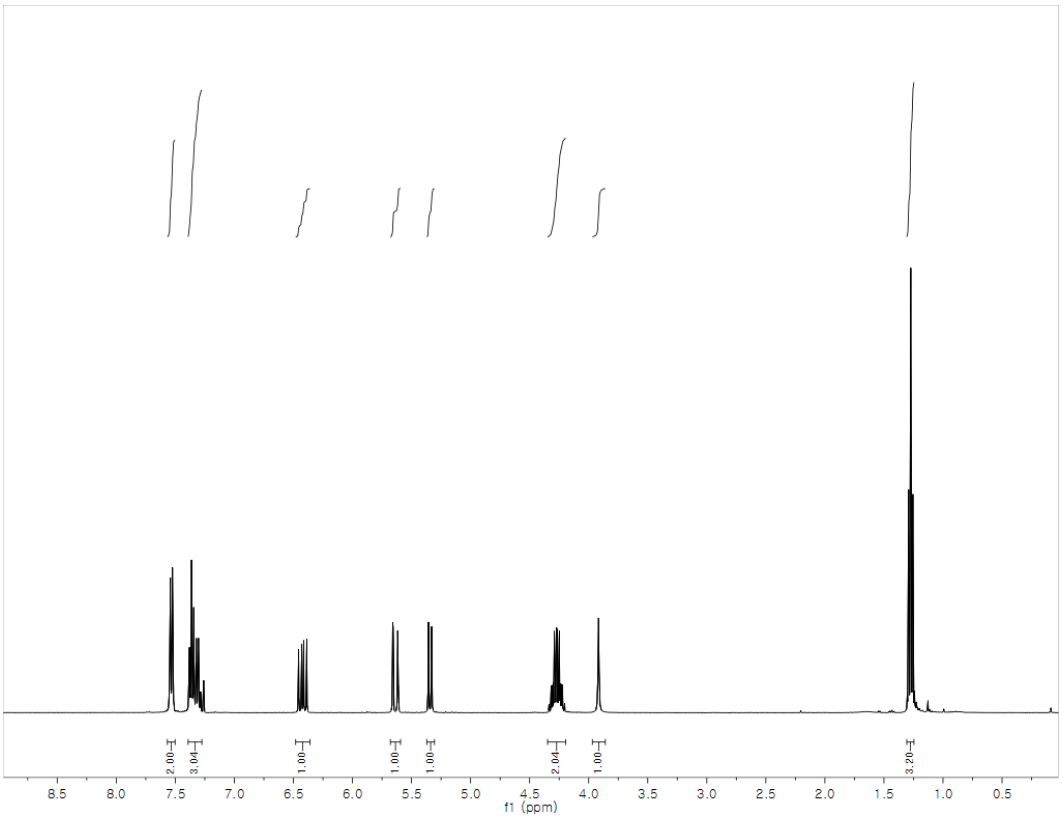
R_f: 0.49 (EtOAc:hexanes = 1:4).

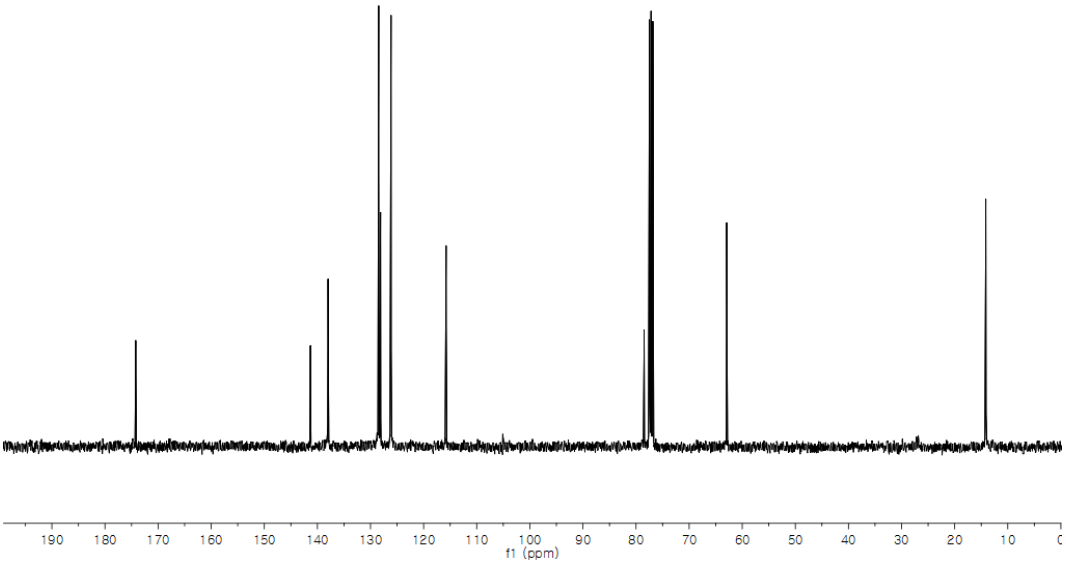
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 2H), 7.38–7.28 (m, 3H), 6.42 (dd, *J* = 17.0 Hz, 10.6 Hz, 1H), 5.64 (dd, *J* = 16.8 Hz, 1.2 Hz, 1H), 5.34 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.34–4.20 (m, 2H), 3.92 (s, 1H), 1.27 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 141.3, 138.0, 128.5, 128.1, 126.1, 115.8, 78.5, 62.9, 14.1.

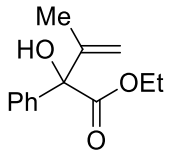
LRMS (ESI) Calcd. for $C_{12}H_{14}O_3$ $[M+Na]^+$: 229, Found: 229.

FTIR (neat): 3501, 2984, 1724.


2.00
3.04
1.00
1.00
1.00
2.04
1.00
3.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Ethyl 2-hydroxy-3-methyl-2-phenylbut-3-enoate (2.3b).



Using Prop-1-en-2-yl pivalate (*O*-Piv-2.2b)

The reaction was conducted at 150 °C for a 40 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 2% EtOAc/hexanes to 3% EtOAc/hexanes) provided the title compound (35.1 mg, 53%) as a pale yellow oil.

Using Prop-1-en-2-yl 2,2,2-triphenylacetate (*O*-TPA-2.2b)

The reaction was conducted at 150 °C for a 40 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 2% EtOAc/hexanes to 3% EtOAc/hexanes) provided the title compound (52.9 mg, 80%) as a pale yellow oil.

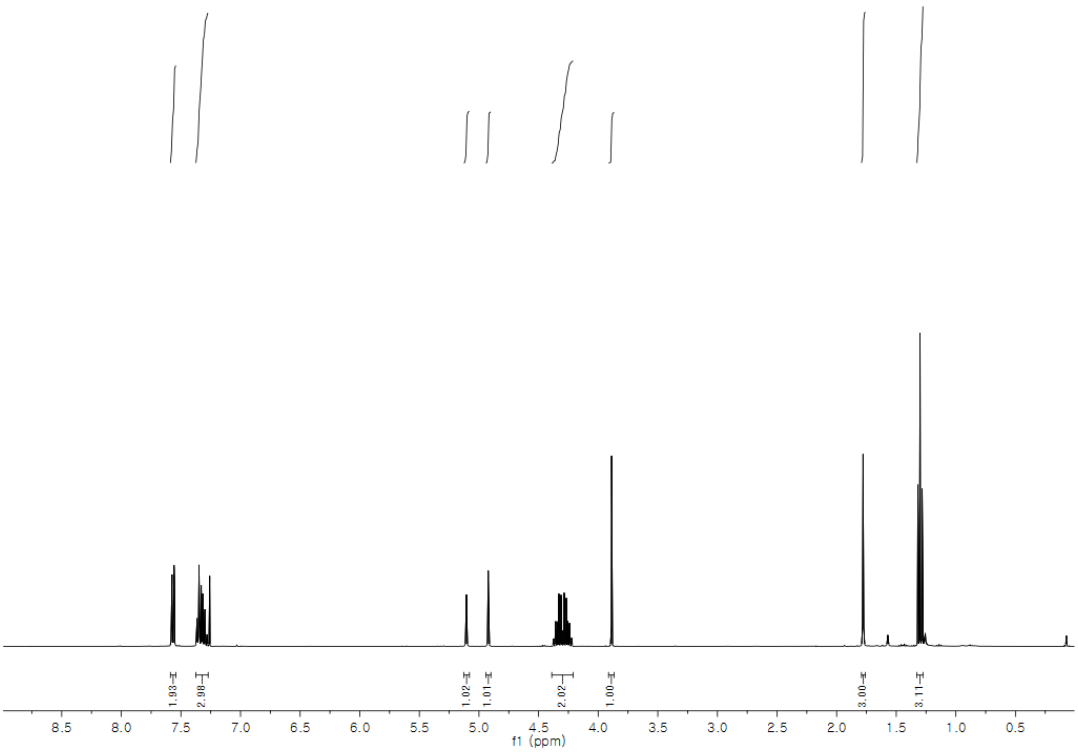
R_f: 0.51 (EtOAc:hexanes = 1:4).

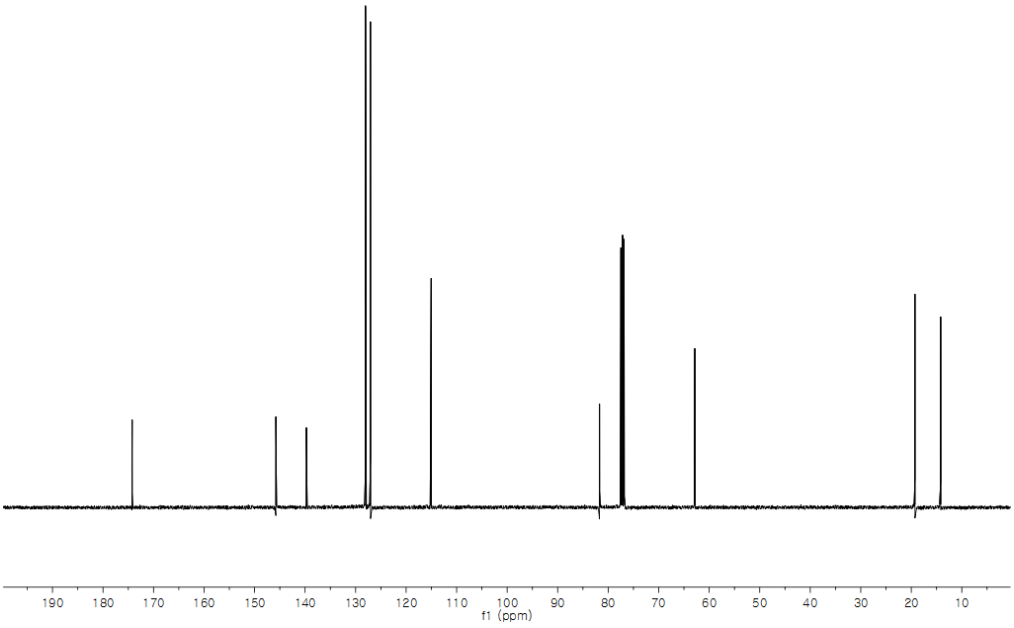
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.55 (m, 2H), 7.37–7.28 (m, 3H), 5.11–5.10 (m, 1H), 4.92 (dd, *J* = 0.8 Hz, 0.8 Hz, 1H), 4.37–4.22 (m, 2H), 3.89 (d, *J* = 2.0 Hz, 1H), 1.78 (dd, *J* = 1.2 Hz, 0.8 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 145.8, 139.7, 128.04, 127.97, 127.1, 115.0, 81.7, 62.8, 19.3, 14.2.

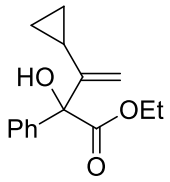
LRMS (ESI) Calcd. for $C_{13}H_{16}O_3$ $[M+Na]^+$: 243, Found: 243.

FTIR (neat): 3495, 2981, 1721.


1.93
2.98
1.02
1.01
2.02
1.00
3.00
3.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Ethyl 3-cyclopropyl-2-hydroxy-2-phenylbut-3-enoate (2.3c).



The reaction was conducted at 140 °C for a 40 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 2% EtOAc/hexanes to 2.5% EtOAc/hexanes) provided the title compound (48.0 mg, 65%) as a pale yellow oil.

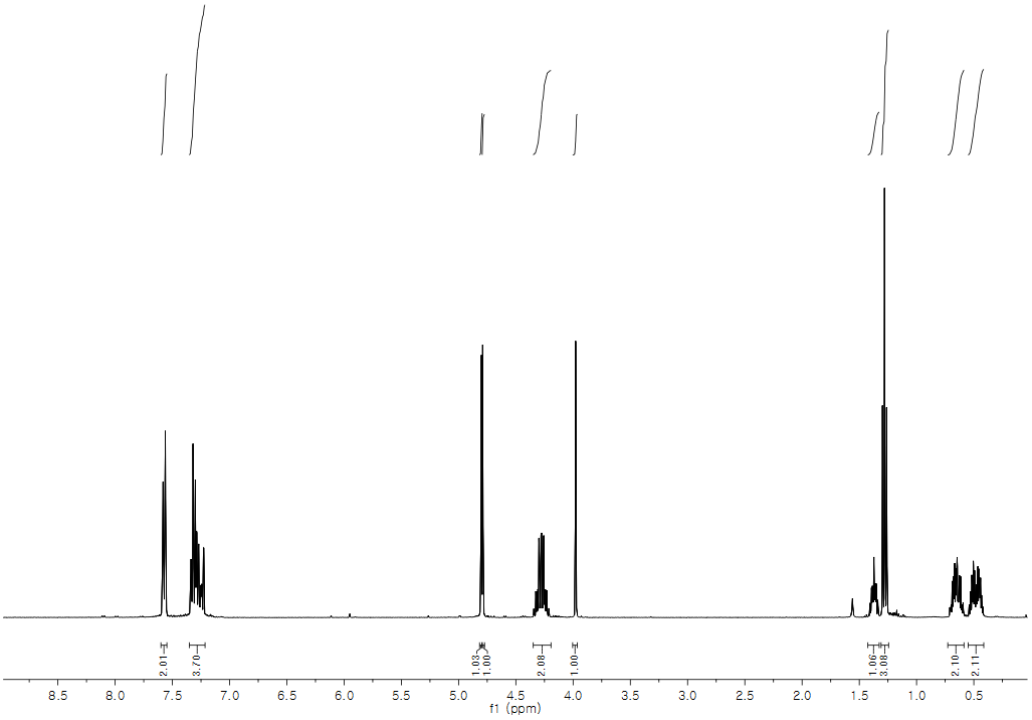
R_f: 0.60 (EtOAc:hexanes = 1:4).

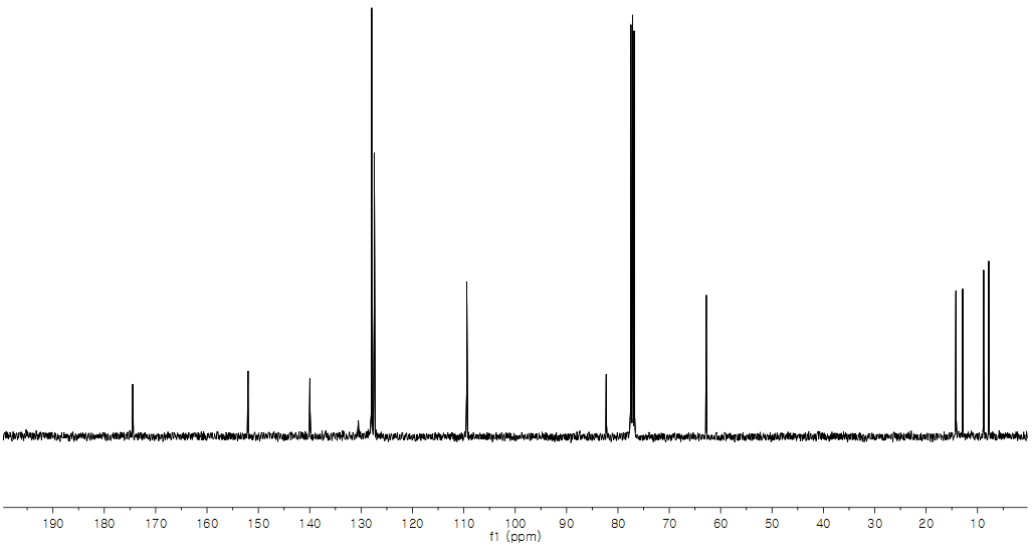
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.34–7.23 (m, 3H), 4.80 (s, 1H), 4.79 (d, *J* = 0.8 Hz, 1H), 4.34–4.21 (m, 2H), 3.98 (d, *J* = 1.2 Hz, 1H), 1.41–1.34 (m, 1H), 1.28 (td, *J* = 7.2 Hz, 1.2 Hz, 3H), 0.71–0.59 (m, 2H), 0.54–0.42 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 152.0, 140.0, 130.5, 128.0, 127.4, 109.4, 82.3, 62.8, 14.2, 12.9, 8.8, 7.8.

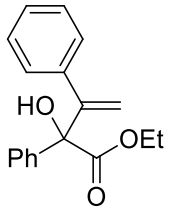
LRMS (CI) Calcd. for $C_{15}H_{18}O_3$ $[M\text{-}OH]^+$: 229, Found: 229.

FTIR (neat): 3497, 1721.


2.01
3.70
1.03
1.00
2.08
1.00
1.06
3.08
2.10
2.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Ethyl 2-hydroxy-2,3-diphenylbut-3-enoate (2.3d).



The reaction was conducted at 150 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 40% DCM/hexanes to 60% DCM/hexanes) provided the title compound (60.1 mg, 71%) as a pale yellow oil.

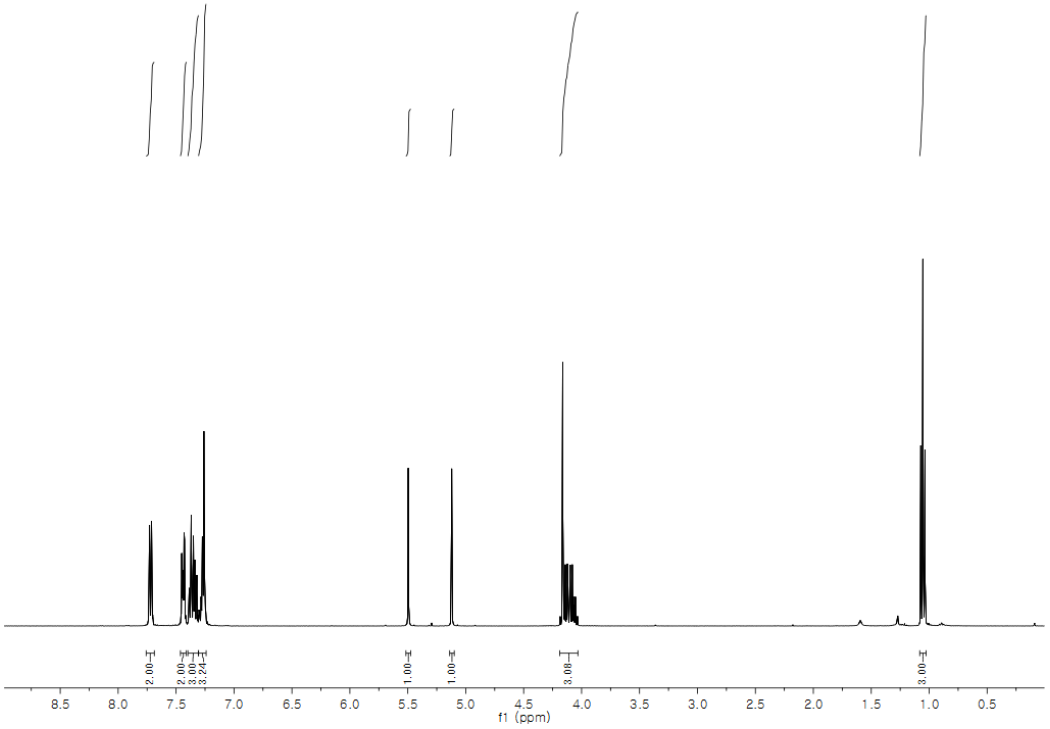
R_f: 0.49 (EtOAc:hexanes = 1:4).

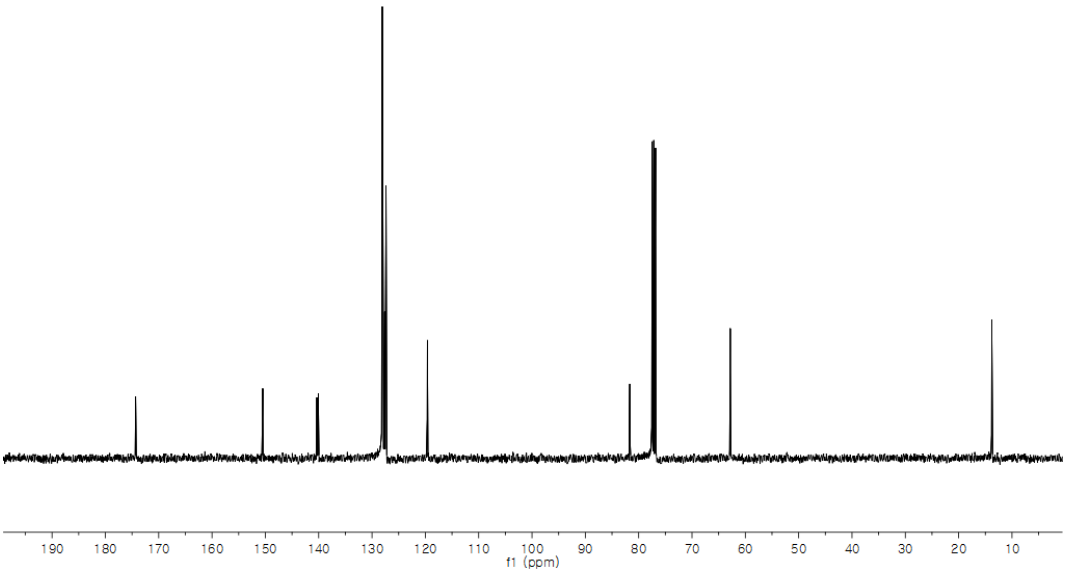
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 2H), 7.45–7.43 (m, 2H), 7.39–7.30 (m, 3H), 7.28–7.25 (m, 3H), 5.50 (d, *J* = 0.4 Hz, 1H), 5.12 (d, *J* = 0.4 Hz, 1H), 4.17–4.05 (m, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 150.5, 140.3, 140.1, 128.1, 128.02, 127.98, 127.6, 127.4, 119.6, 81.7, 62.8, 13.8 (1 missing carbon).

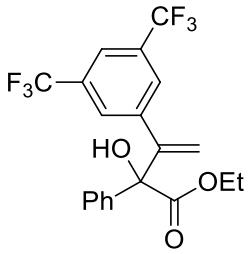
LRMS (ESI) Calcd. for $C_{18}H_{18}O_3$ $[M+Na]^+$: 305, Found: 305.

FTIR (neat): 3483, 2980, 1721.


2.00
2.00
3.00
3.24
1.00
1.00
3.08
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Ethyl 3-(3,5-bis(trifluoromethyl)phenyl)-2-hydroxy-2-phenylbut-3-enoate (2.3e).



The reaction was conducted at 150 ºC for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 30% DCM/hexanes to 35% DCM/hexanes) provided the title compound (100.4 mg, 80%) as a pale yellow oil.

R_f: 0.22 (EtOAc:hexanes = 1:4).

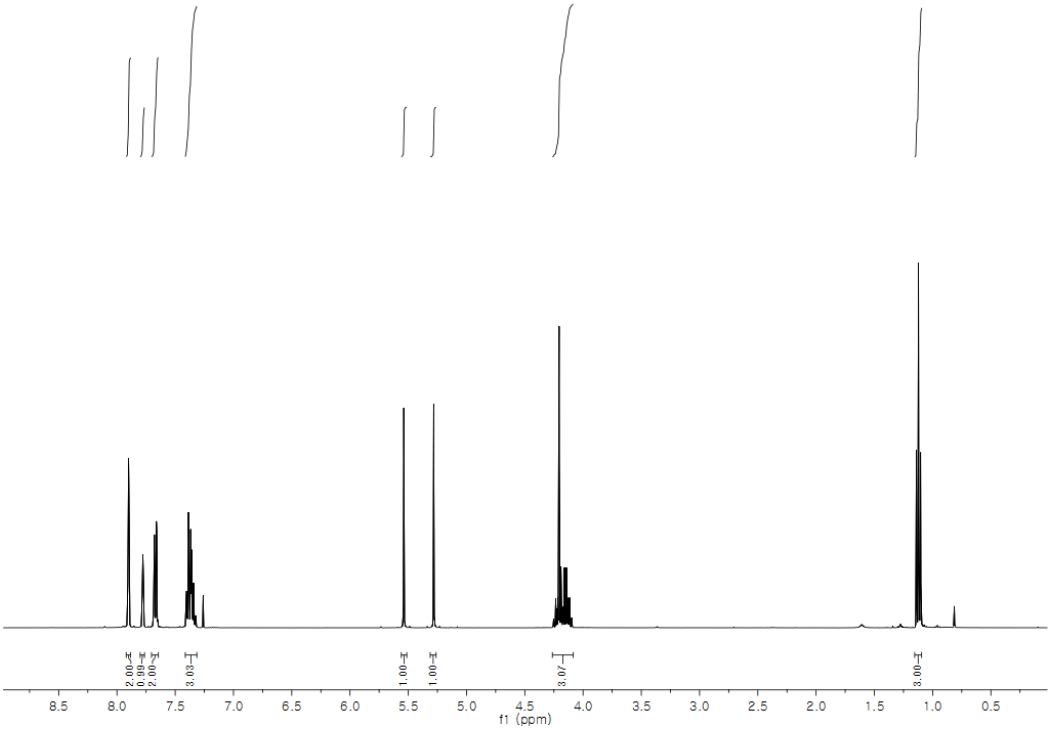
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 2H), 7.78 (s, 1H), 7.68–7.65 (m, 2H), 7.40–7.34 (m, 3H), 5.54 (s, 1H), 5.28 (s, 1H), 4.25–4.10 (m, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

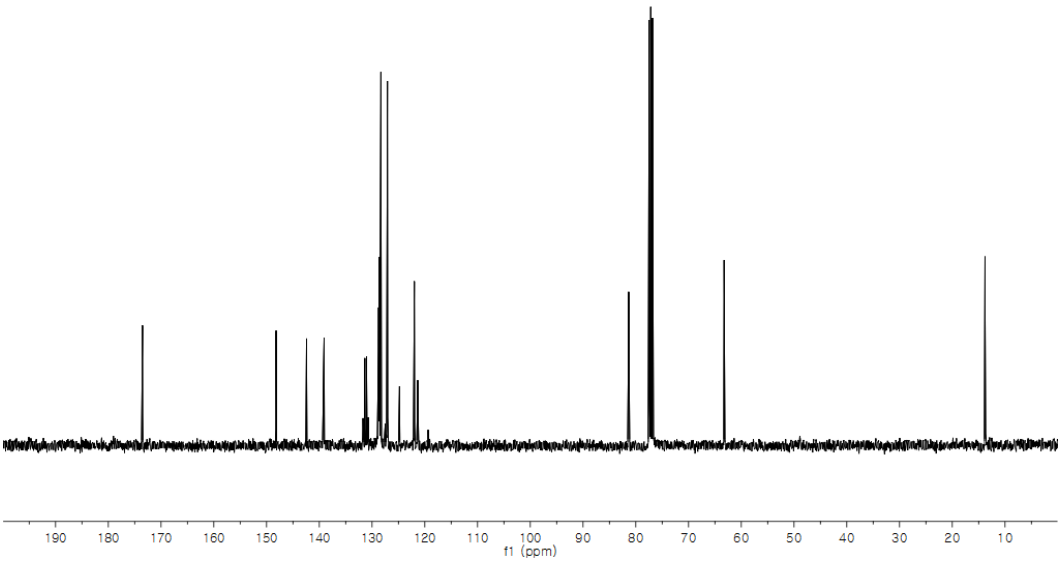
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 148.2, 142.4, 139.1, 131.2 (quartet, *J* = 33.0 Hz), 128.8, 128.6, 128.3, 127.1, 126.2 (quartet, *J* = 271.3 Hz), 122.0, 121.3, 81.4, 63.3, 13.8.

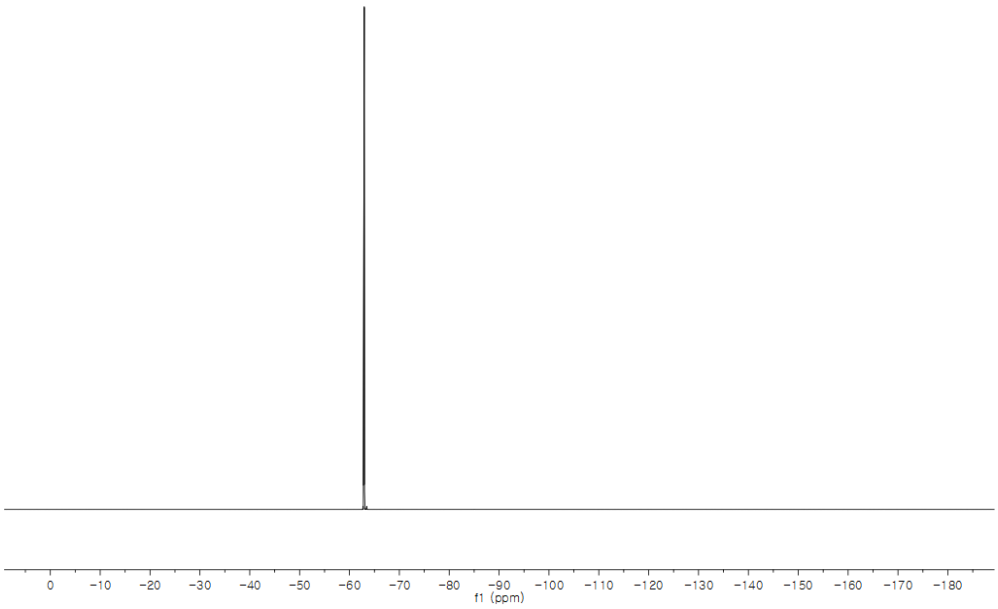
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0.

LRMS (CI) Calcd. for $C_{20}H_{16}F_6O_3$ $[M\text{-}OH]^+$: 401, Found: 401.

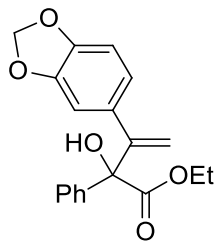
FTIR (neat): 3482, 1728.


2.00
0.99
2.00
3.03
1.00
1.00
3.07
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)

Ethyl 3-(benzo[*d*][1,3]dioxol-5-yl)-2-hydroxy-2-phenylbut-3-enoate (2.3f).



The reaction with Os_3CO_{12} (10.9 mg, 4 mol%) and XPhos (35.4 mg, 24 mol%) was conducted at 150 ^oC for a 72 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 4% EtOAc/hexanes) provided the title compound (44.1 mg, 45%) as a pale yellow oil and starting material was recovered (27.0 mg, 50%).

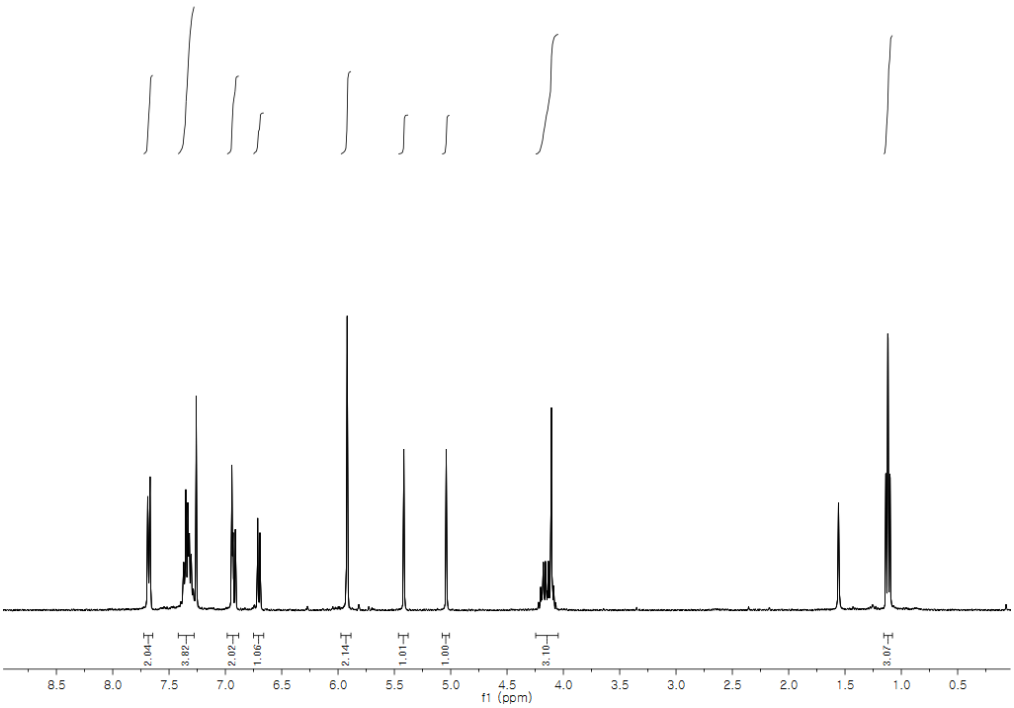
R_f: 0.31 (EtOAc:hexanes = 1:4).

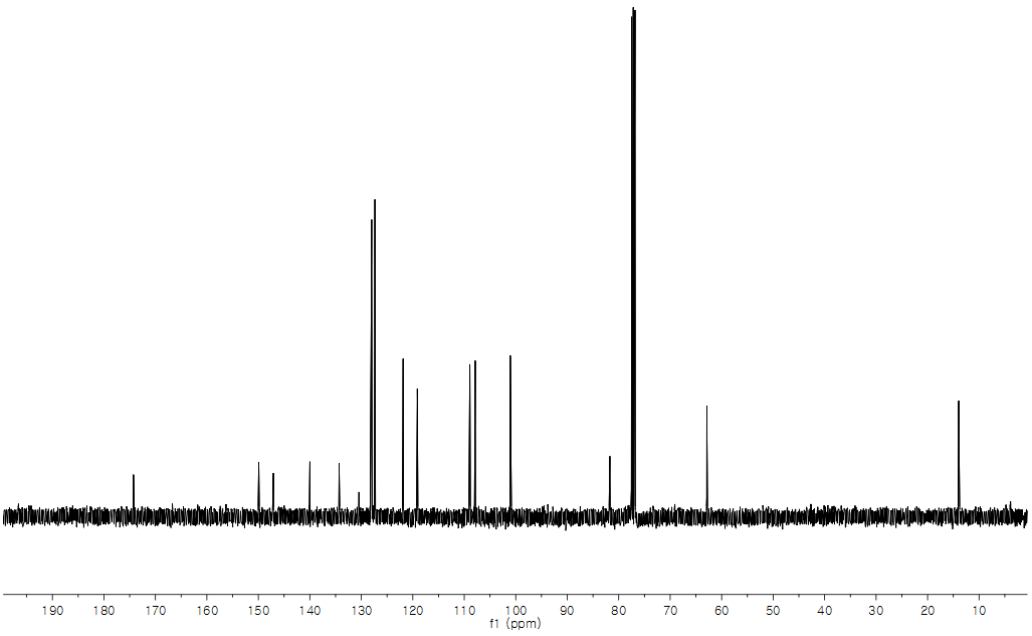
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.42–7.28 (m, 4H), 6.98–6.88 (m, 2H), 6.70 (dd, *J* = 8.0 Hz, 0.7 Hz, 1H), 5.97–5.89 (m, 2H), 5.42 (s, 1H), 5.04 (s, 1H), 4.25–4.05 (m, 3H), 1.12 (td, *J* = 7.1 Hz, 1.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 149.9, 147.2, 147.1, 140.0, 134.3, 128.1, 128.0, 127.4, 121.9, 119.1, 108.9, 107.9, 101.1, 81.7, 62.9, 14.0.

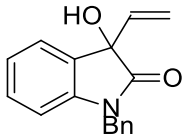
LRMS (ESI) Calcd. for $C_{19}H_{18}O_5$ $[M+Na]^+$: 349, Found: 349.

FTIR (neat): 2982, 1722.


2.04
3.82
2.02
1.06
2.14
1.01
1.00
3.10
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-hydroxy-3-vinylindolin-2-one (2.4a).



The reaction was conducted at 130 °C for a 4 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (78.8 mg, 99%) as a brown solid.

R_f: 0.11 (EtOAc:hexanes = 1:4).

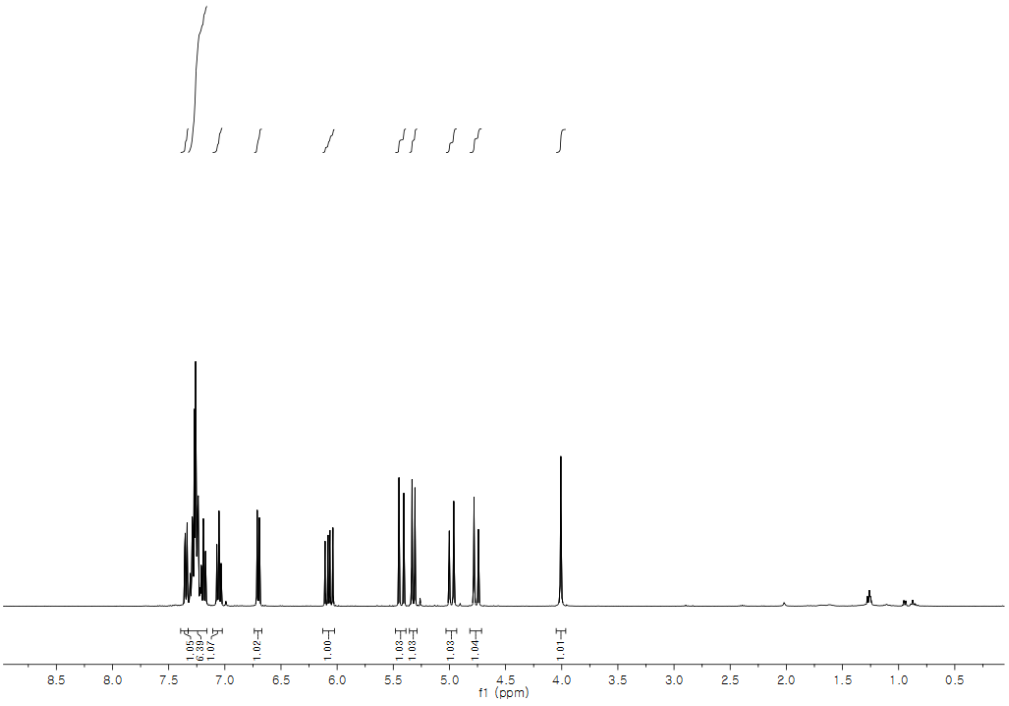
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.17 (m, 7H), 7.06 (dd, *J* = 7.2 Hz, 7.2 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.07 (dd, *J* = 17.0 Hz, 10.6 Hz, 1H) 5.43 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.01 (s, 1H).

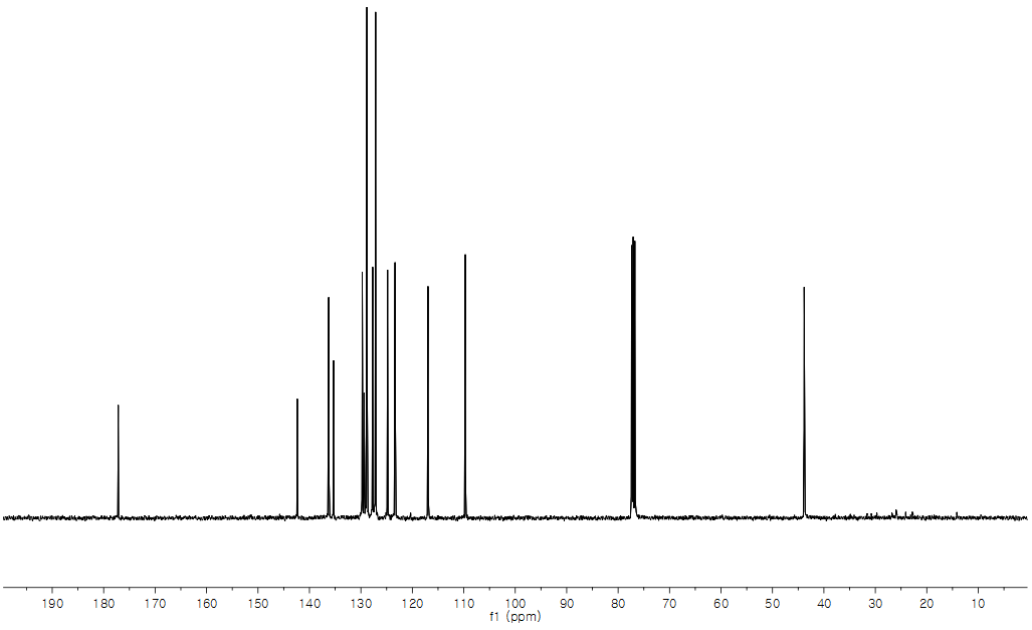
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 142.5, 136.4, 135.4, 129.8, 129.5, 128.9, 127.8, 127.2, 124.9, 123.5, 117.0, 109.8, 77.3, 43.9.

LRMS (CI) Calcd. for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266, Found: 266.

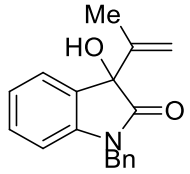
FTIR (neat): 3389, 1705, 1614.

MP: 128 °C.


1.05
6.39
1.07
1.02
1.00
1.03
1.03
1.03
1.04
1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-hydroxy-3-(prop-1-en-2-yl)indolin-2-one (2.4b).



The reaction was conducted at 130 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (71.2 mg, 85%) as a yellow solid.

R_f: 0.20 (EtOAc:hexanes = 1:4)

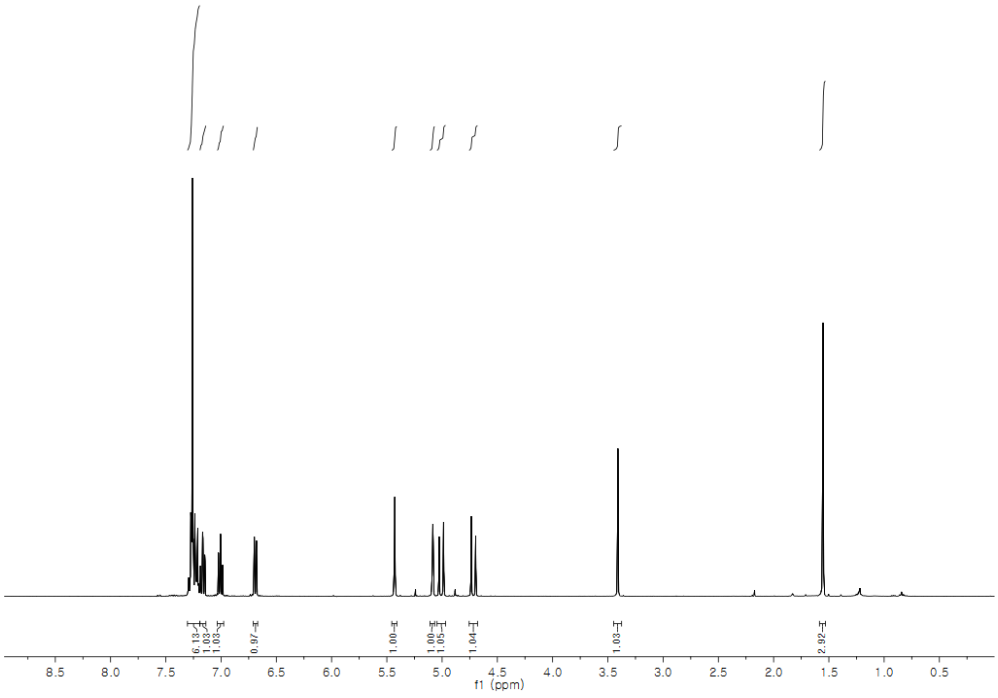
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.15 (m, 6H), 7.17 (ddd, *J* = 7.8 Hz, 7.8 Hz, 1.2 Hz, 1H), 7.00 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.0 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.430-5.426 (m, 1H), 5.09–5.08 (m, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.72 (d, *J* = 15.6 Hz, 1H), 3.41 (s, 1H), 1.55 (dd, *J* = 1.6 Hz, 0.8 Hz, 3H).

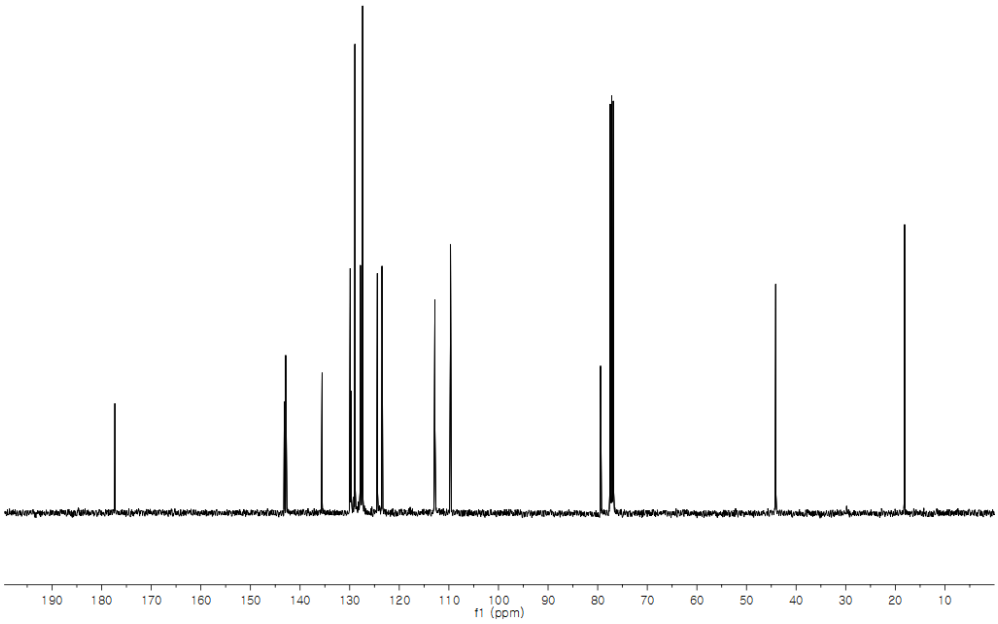
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 143.2, 142.9, 135.6, 129.9, 129.7, 128.9, 127.8, 127.4, 124.4, 123.5, 112.8, 109.7, 79.4, 44.1, 18.1.

LRMS (CI) Calcd. for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280, Found: 280.

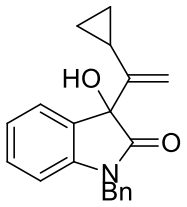
FTIR (neat): 3390, 1702, 1612.

MP: 134 °C.


6.13
1.03
1.03
0.97
1.00
1.00
1.05
1.04
1.03
2.92
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-(1-cyclopropylvinyl)-3-hydroxyindolin-2-one (2.4c).



Using 1-Cyclopropylvinyl pivalate (*O*-Piv-2.2c)

The reaction was conducted at 130 ^{o}C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (55.0 mg, 60%) as a yellow solid.

Using 1-Cyclopropylvinyl 2,2,2-triphenylacetate (*O*-TPA-2.2c)

The reaction was conducted at 130 ^{o}C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (77.9 mg, 85%) as a yellow solid.

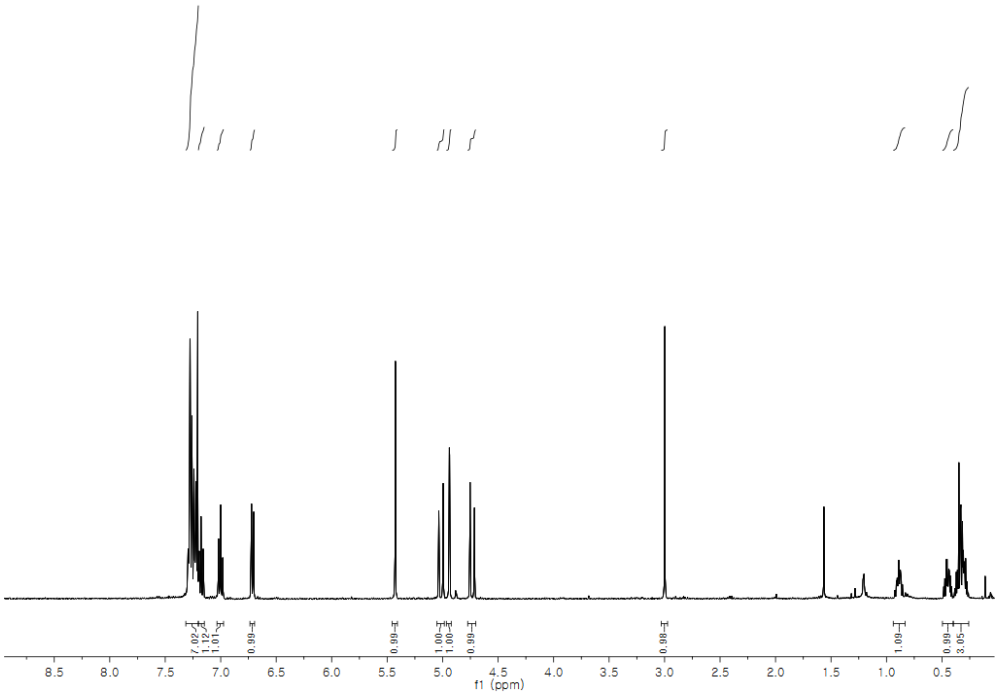
R_f: 0.19 (EtOAc:hexanes = 1:4)

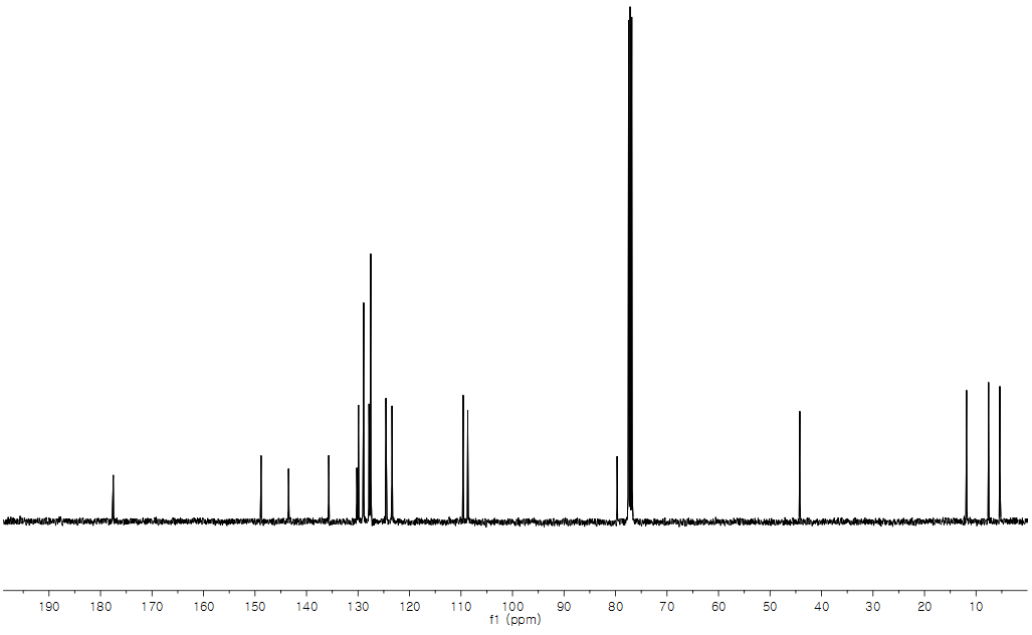
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.21 (m, 7H), 7.18 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.0 Hz, 1H), 7.00 (dd, *J* = 7.4 Hz, 7.4 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 5.43 (s, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.94 (s, 1H), 4.73 (d, *J* = 15.6 Hz, 1H), 3.00 (s, 1H), 0.92–0.83 (m, 1H), 0.48–0.41 (m, 1H), 0.39–0.26 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.5, 148.8, 143.5, 135.7, 130.2, 129.9, 128.9, 127.9, 127.5, 124.6, 123.4, 109.6, 108.7, 79.7, 44.2, 11.9, 7.6, 5.4.

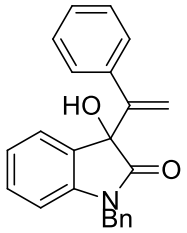
LRMS (ESI) Calcd. for $C_{20}H_{19}NO_2$ $[M+Na]^+$: 328, Found: 328.

FTIR (neat): 3355, 3006, 1630. **MP**: 142 ^{o}C.


7.02
1.12
1.01
0.99
0.99
1.00
1.00
0.99
0.98
1.09
0.99
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-hydroxy-3-(1-phenylvinyl)indolin-2-one (2.4d).



The reaction was conducted at 130 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (89.1 mg, 87%) as a white solid.

R_f: 0.16 (EtOAc:hexanes = 1:4).

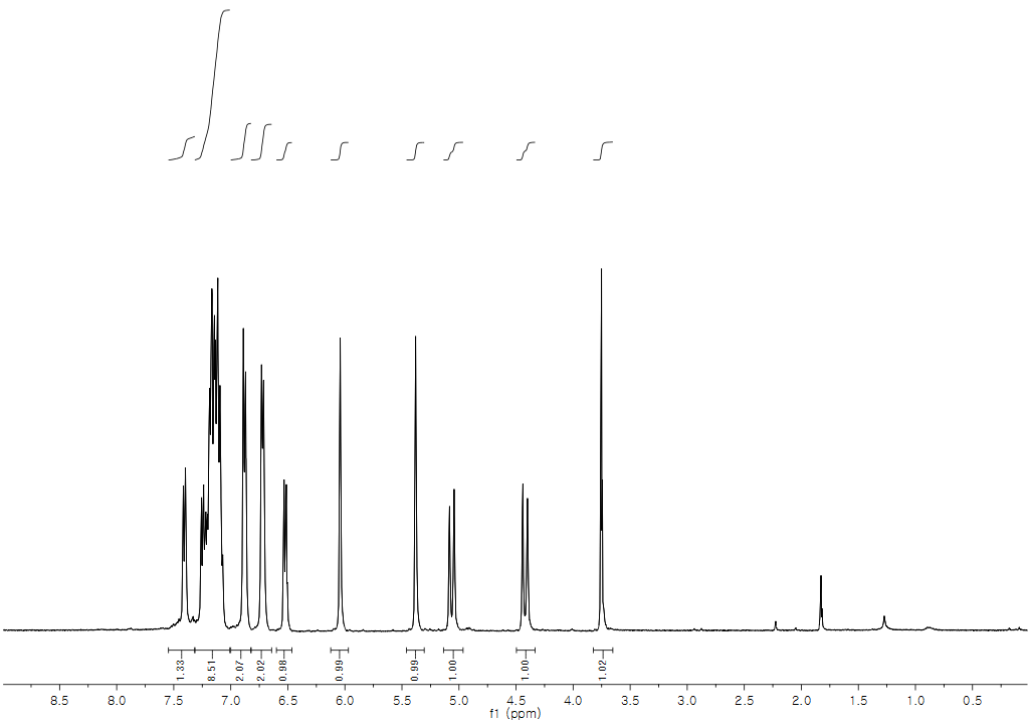
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.26–7.07 (m, 8H), 6.89–6.86 (m, 2H), 6.72 (d, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.04 (s, 1H), 5.38 (s, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.42 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 1H).

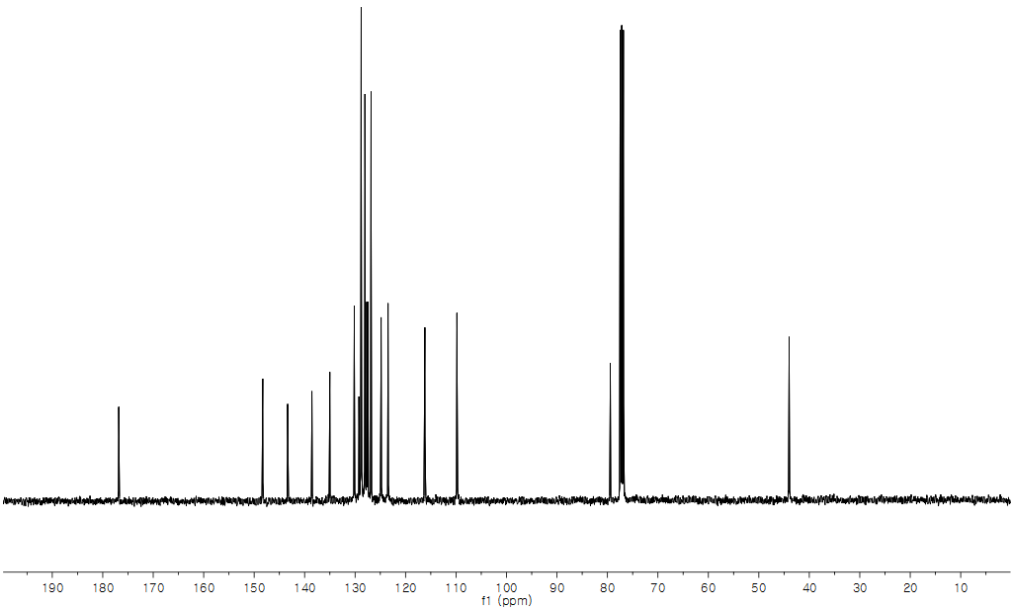
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 148.3, 143.4, 138.6, 135.0, 130.2, 128.80, 128.77, 128.0, 127.7, 127.5, 126.8, 123.5, 116.2, 109.8, 79.4, 44.0 (2 missing carbons).

LRMS (ESI) Calcd. for $C_{23}H_{19}NO_2$ $[M+Na]^+$: 364, Found: 364.

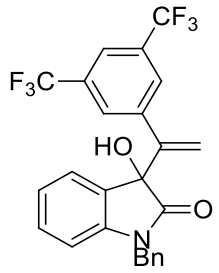
FTIR (neat): 3390, 1702, 1612.

MP: 150 °C.


1.33
8.51
2.07
2.02
0.98
0.99
0.99
1.00
1.00
1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)-3-hydroxyindolin-2-one (2.4e).



The reaction was conducted at 130 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (134.6 mg, 94%) as a yellow solid.

R_f: 0.26 (EtOAc:hexanes = 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.36 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.26–7.22 (m, 3H), 7.19–7.10 (m, 4H), 6.80 (d, *J* = 6.8 Hz, 2H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.10 (s, 1H), 5.41 (s, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.48 (d, *J* = 15.6 Hz, 1H), 4.27 (s, 1H).

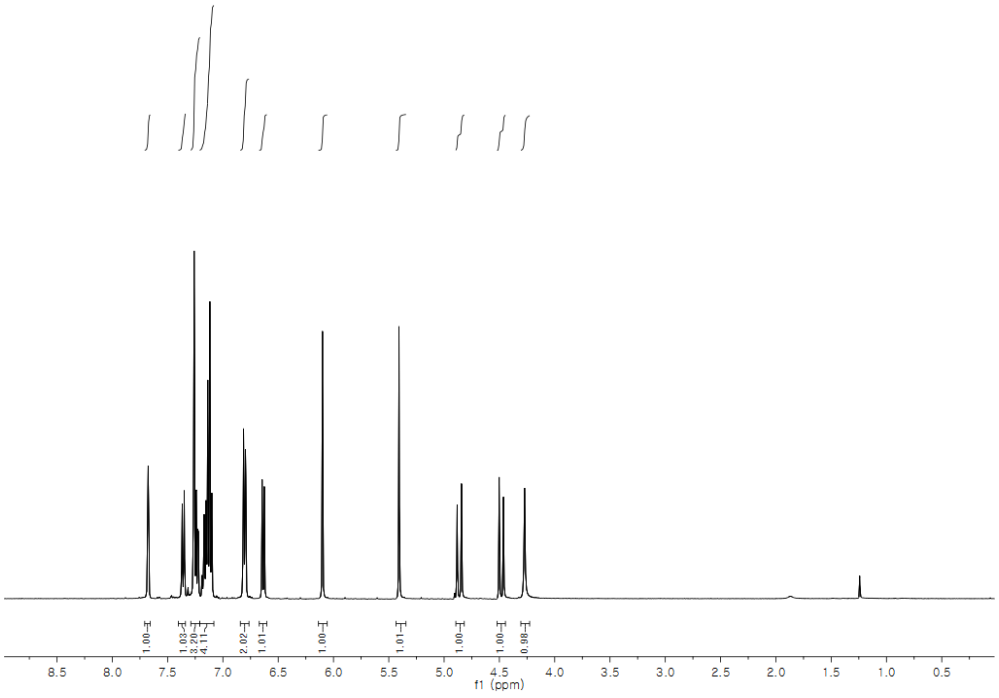
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 146.2, 143.1, 140.6, 134.8, 131.2 (q, *J* = 33.0 Hz), 130.7, 129.0, 128.8, 128.4, 127.8, 126.9, 124.9, 124.0, 123.1 (q, *J* = 271.0 Hz,), 121.73, 121.66, 118.5, 110.1, 79.2, 77.5, 77.2, 76.8, 44.1 (1 missing carbon).

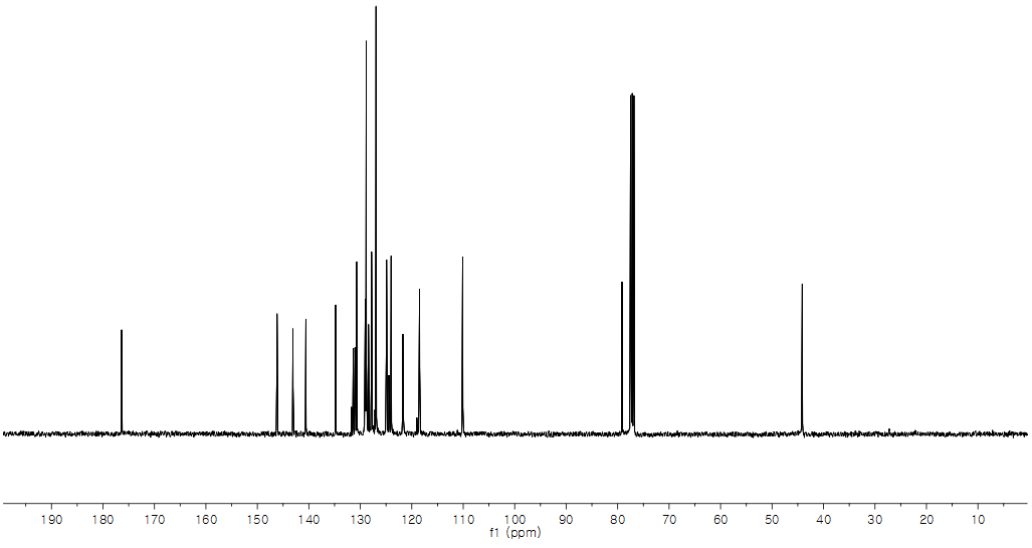
^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0.

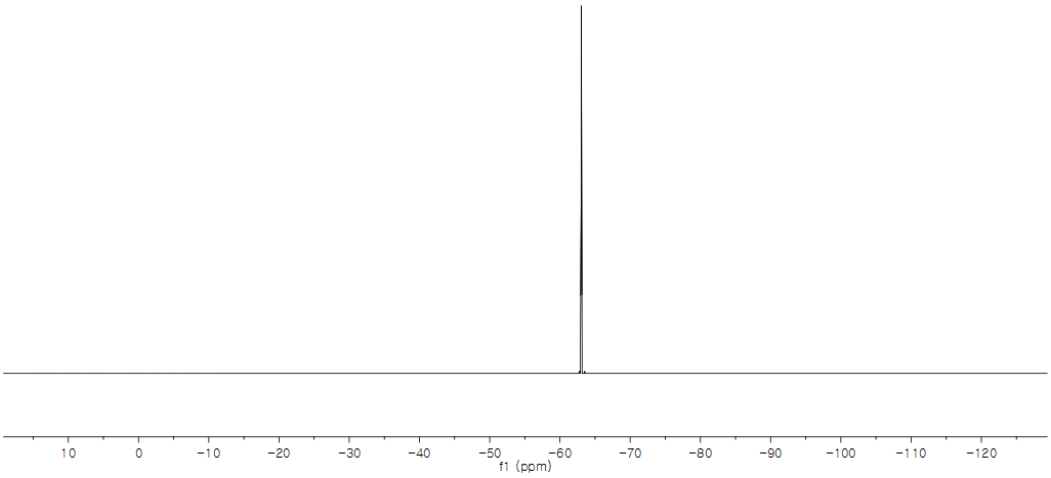
LRMS (CI) Calcd. for $C_{25}H_{17}F_6NO_2$ $[M+H]^+$: 478, Found: 478.

FTIR (neat): 3394, 3308, 1692.

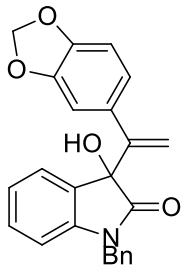
MP: 154 °C.


1.00
1.03
3.20
4.11
2.02
1.01
1.00
1.01
1.00
1.00
0.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
f1 (ppm)

3-(1-(Benzo[*d*][1,3]dioxol-5-yl)vinyl)-1-benzyl-3-hydroxyindolin-2-one (2.4f).



The reaction was conducted at 130 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (104.1 mg, 90%) as a white solid.

R_f: 0.11 (EtOAc:hexanes = 1:4).

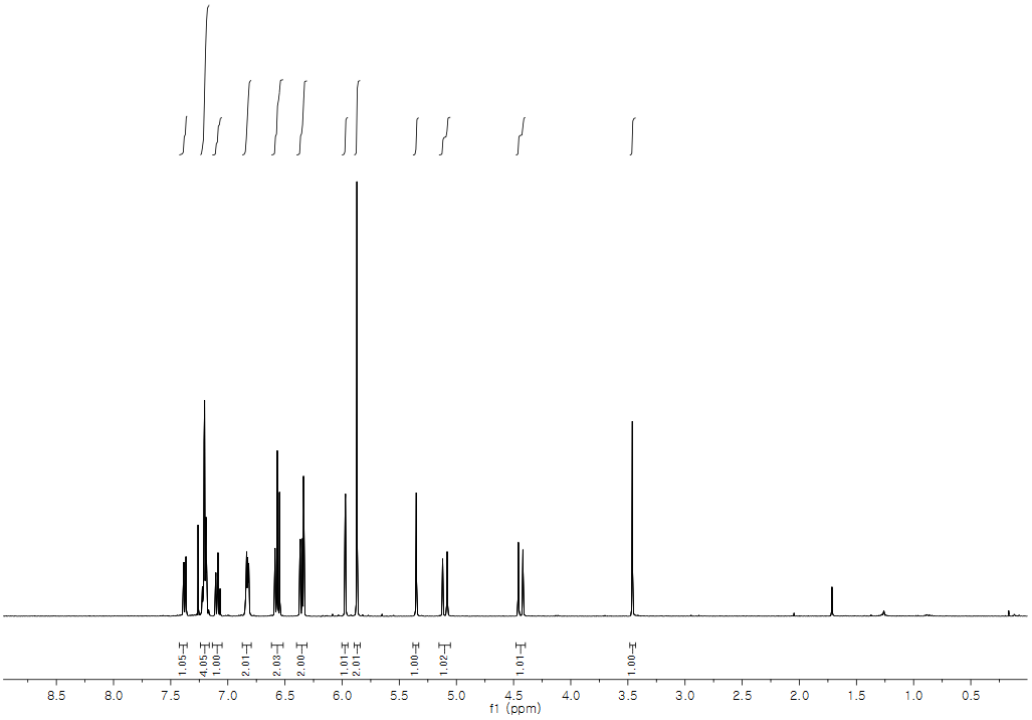
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.23–7.18 (m, 4H), 7.09 (ddd, *J* = 7.6 Hz, 7.6 Hz, 0.7 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 4.0 Hz, 1H), 6.57 (dd, *J* = 7.8 Hz, 7.8 Hz, 2H), 6.37–6.33 (m, 2H), 5.97 (d, *J* = 0.8 Hz, 1H), 5.87 (s, 2H), 5.35 (d, *J* = 0.8 Hz, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 3.46 (s, 1H).

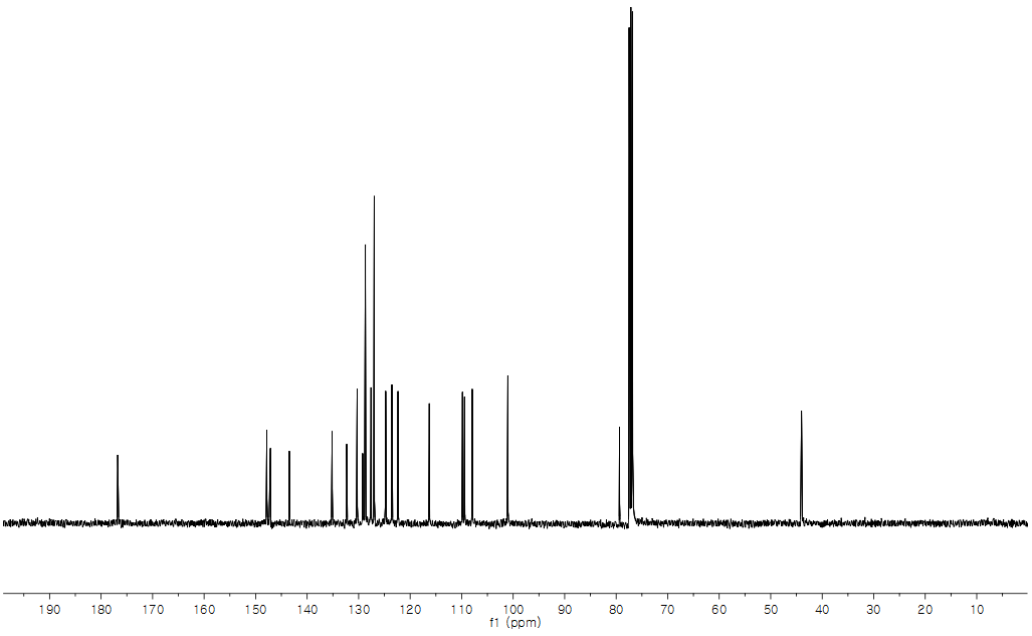
^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 147.8, 147.2, 147.1, 143.5, 135.1, 132.3, 130.3, 129.2, 128.7, 127.6, 127.0, 124.8, 123.5, 122.4, 116.3, 109.8, 109.4, 108.0, 101.0, 79.4, 44.0.

LRMS (CI) Calcd. for $C_{24}H_{19}NO_4$ $[M+H]^+$: 386, Found: 386.

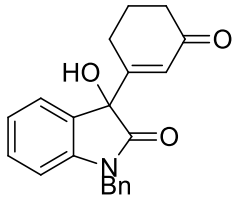
FTIR (neat): 3383, 3057, 1703.

MP: 152 °C.


1.05
4.05
1.00
2.01
2.03
2.00
1.01
2.01
1.00
1.02
1.01
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

1-Benzyl-3-hydroxy-3-(1-(3-oxocyclohex-1-en-1-yl)vinyl)indolin-2-one (2.4g).



The reaction was conducted at 130 ^{o}C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 30% EtOAc/hexanes) provided the title compound (73.0 mg, 73%) as a yellow solid.

R_f: 0.07 (EtOAc:hexanes = 1:4).

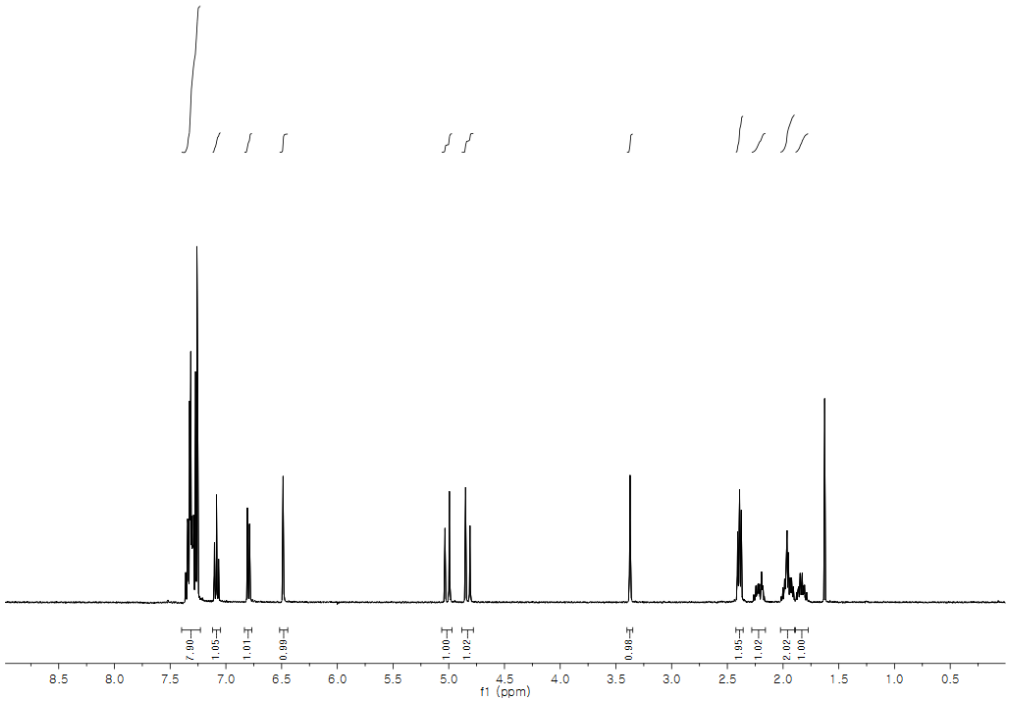
^{1}H NMR (400 MHz, $CDCl_3$): 7.40–7.23 (m, 7H), 7.12–7.05 (m, 1H), 6.83–6.77 (m, 1H), 6.49 (s, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.37 (s, 1H), 2.42–2.36 (m, 2H), 2.28–2.16 (m, 1H), 2.02–1.90 (m, 2H), 1.89–1.78 (m, 1H).

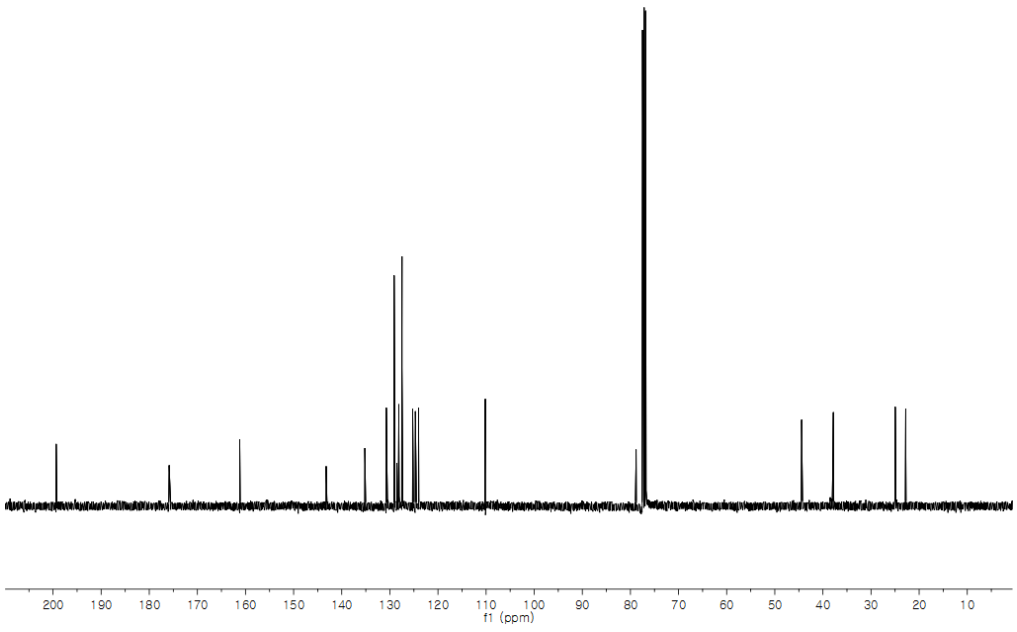
^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 175.9, 161.2, 143.2, 135.2, 130.7, 129.1, 128.5, 128.1, 127.5, 125.3, 124.7, 124.0, 110.2, 78.8, 44.4, 37.8, 25.0, 22.8.

LRMS (ESI) Calcd. for $C_{21}H_{19}NO_3$ $[M+Na]^+$: 356, Found: 356.

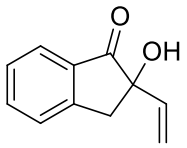
FTIR (neat): 3337, 3059, 1714.

MP: 190 ^{o}C.


7.00
1.05
1.01
0.99
1.00
1.02
0.98
1.95
1.02
2.02
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-hydroxy-2-vinyl-2,3-dihydro-1*H*-inden-1-one (2.5a).



The reaction was conducted with 500 mol% of vinyl pivalate at 130 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 5% EtOAc/hexanes to 10% EtOAc/hexanes) provided the title compound (35.0 mg, 67%) as a pale yellow oil.

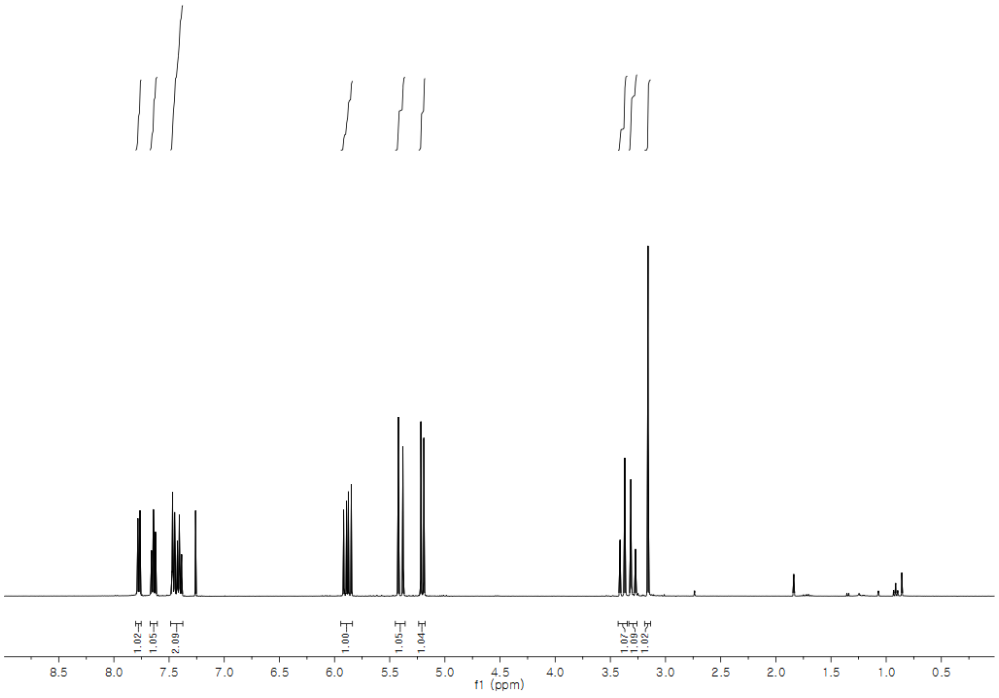
R_f: 0.22 (EtOAc:hexanes = 1:4).

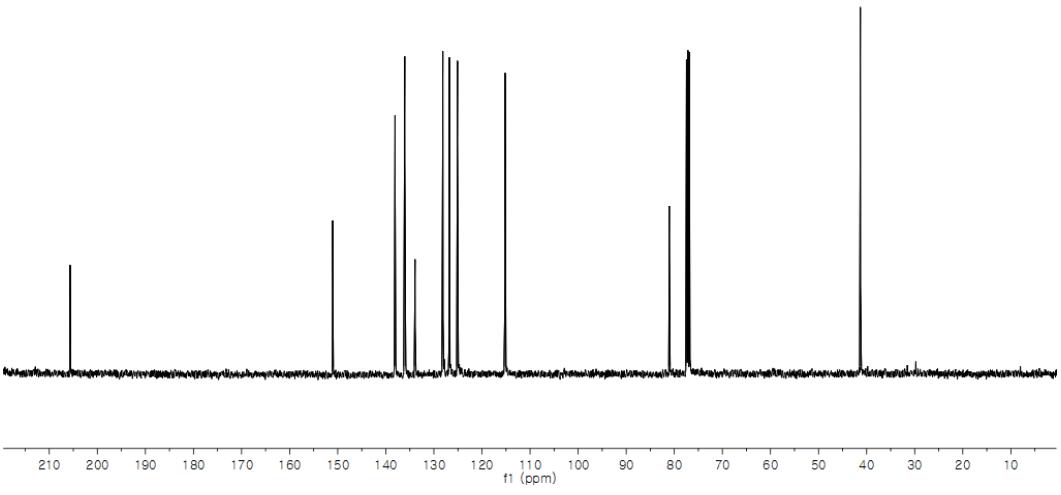
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.45–7.37 (m, 2H), 5.88 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 3.40–3.36 (m, 2H), 3.29 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 151.1, 138.1, 136.1, 133.9, 128.1, 126.8, 125.1, 115.2, 81.0, 41.3.

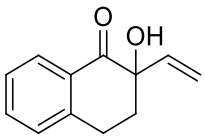
LRMS (ESI) Calcd. for $C_{11}H_{10}O_2$ $[M+Na]^+$: 197, Found: 197.

FTIR (neat): 3430, 1710.


1.02
1.05
2.09
1.00
1.05
1.04
1.07
1.04
1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-Hydroxy-2-vinyl-3,4-dihydronaphthalen-1(2*H*)-one (2.5b).



The reaction was conducted with 500 mol% of vinyl pivalate at 140 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 1% EtOAc/hexanes to 2% EtOAc/hexanes) provided the title compound (39.5 mg, 70%) as a pale yellow oil.

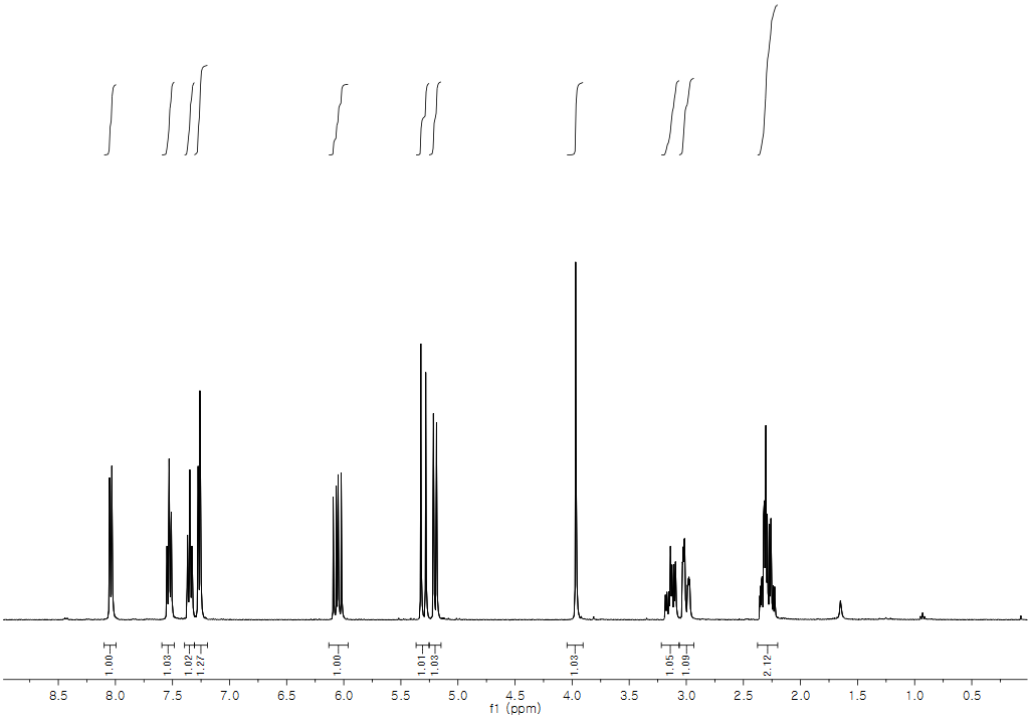
R_f: 0.48 (EtOAc:hexanes = 1:4).

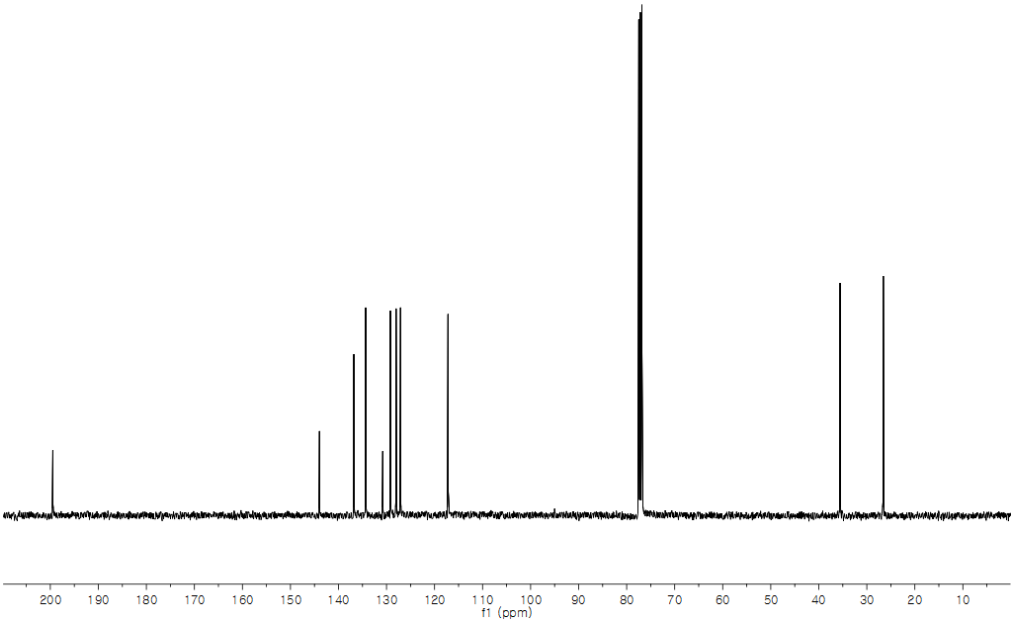
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.53 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.5 Hz, 1H), 7.37–7.33 (m, 1H), 7.27 (dd, *J* = 7.0 Hz, 0.6 Hz, 1H), 6.06 (ddd, *J* = 17.6 Hz, 10.8 Hz, 1.1 Hz, 1H), 5.30 (ddd, *J* = 17.2 Hz, 1.0 Hz, 1.0 Hz, 1H), 5.20 (dd, *J* = 10.8 Hz, 0.8 Hz, 1H), 3.97 (s, 1H), 3.14 (ddd, *J* = 12.6 Hz, 17.6 Hz, 1.3 Hz, 1H), 3.00 (ddd, *J* = 17.4 Hz, 5.0 Hz, 1.8 Hz, 1H), 2.36–2.33 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 144.0, 136.8, 134.3, 130.8, 129.2, 128.0, 127.1, 117.2, 76.9, 35.6, 26.6.

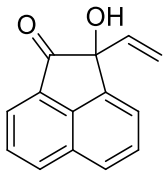
LRMS (CI) Calcd. for $C_{12}H_{12}O_2$ $[M+H]^+$: 189, Found: 189.

FTIR (neat): 3476, 1684.


1.00
1.03
1.02
1.27
1.00
1.01
1.03
1.03
1.05
1.09
2.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-Hydroxy-2-vinylacenaphthylen-1(2*H*)-one (2.5c).



The reaction was conducted with 500 mol% of vinyl pivalate at 150 ^{o}C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 5% EtOAc/hexanes to 10% EtOAc/hexanes) provided the title compound (37.9 mg, 60%) as a white solid.

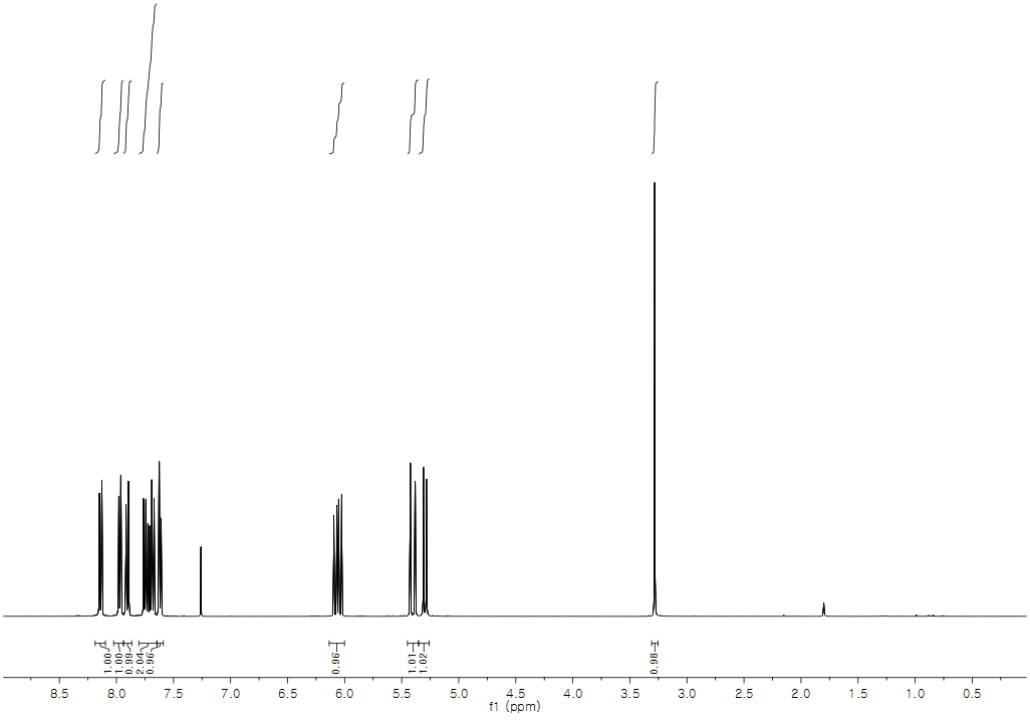
R_f: 0.22 (EtOAc:hexanes = 1:4).

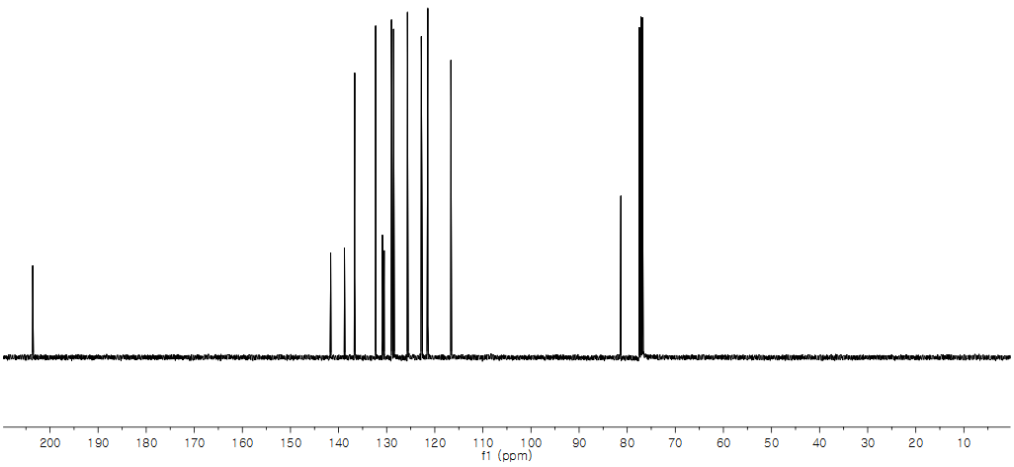
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 6.7 Hz, 1H), 7.92 (dd, *J* = 8.3 Hz, 0.6 Hz, 1H), 7.79–7.67 (m, 2H), 7.65–7.61 (m, 1H), 6.06 (dd, *J* = 17.2 Hz, 10.6 Hz, 1H), 5.42 (dd, *J* = 17.2 Hz, 0.8 Hz, 1H), 5.31 (dd, *J* = 10.6 Hz, 0.7 Hz, 1H), 3.09 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 203.5, 141.7, 138.8, 136.7, 132.3, 131.0, 130.6, 129.0, 128.6, 125.7, 122.8, 121.5, 116.7, 81.3.

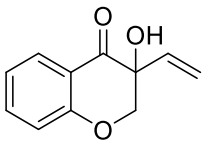
LRMS (ESI) Calcd. for $C_{14}H_{10}O_2$ $[M+Na]^+$: 233, Found: 233.

FTIR (neat): 3386, 1706.


1.00
1.00
0.99
2.04
0.96
0.99
1.01
1.02
0.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3-Hydroxy-2,2-dimethyl-3-vinylchroman-4-one (2.5d).



The reaction was conducted with 500 mol% of vinyl pivalate at 140 °C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 10% EtOAc/hexanes to 20% EtOAc/hexanes) provided the title compound (50.2 mg, 88%) as a colorless oil.

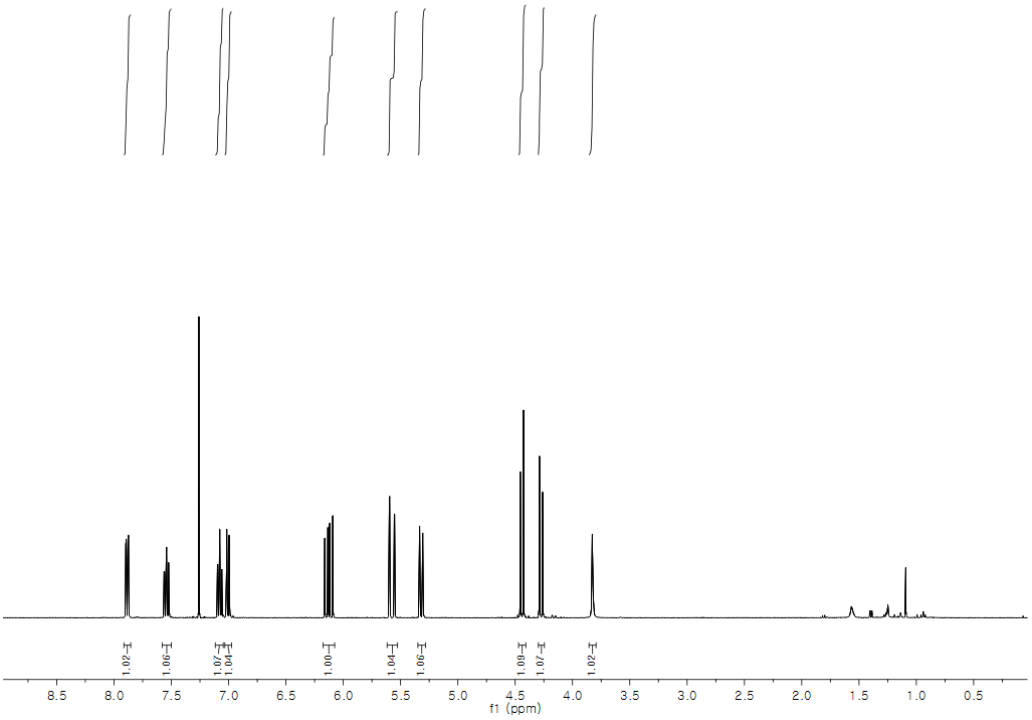
R_f: 0.45 (EtOAc:hexanes = 1:4).

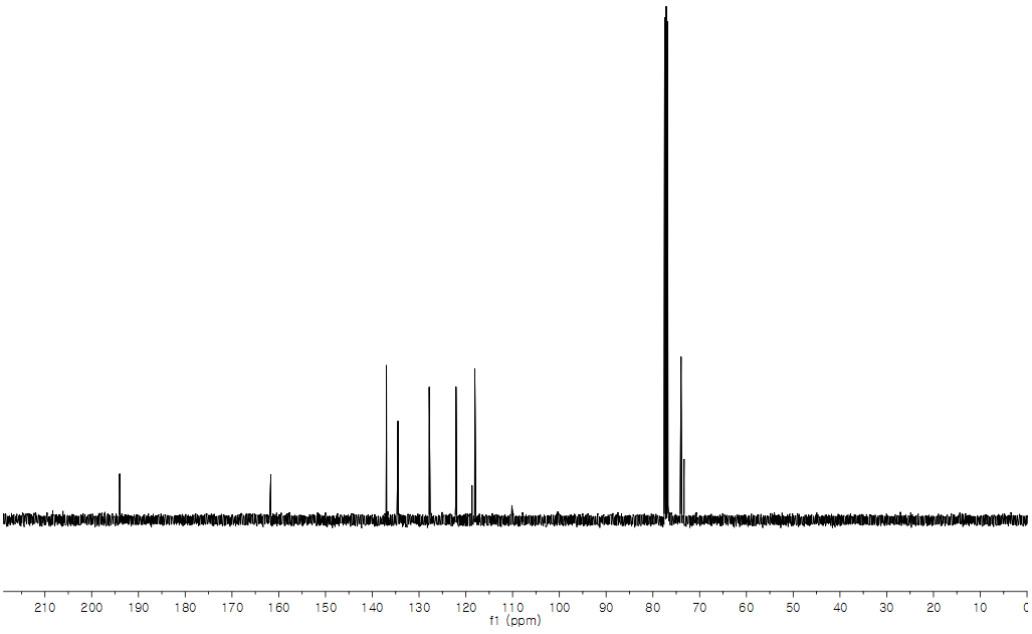
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.85 (m, 1H), 7.54 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.8 Hz, 1H), 7.08 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 7.03–6.97 (m, 1H), 6.13 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.57 (dd, *J* = 17.2 Hz, 0.9 Hz, 1H), 5.35–5.28 (m, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.30–4.24 (m, 1H), 3.83 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 161.7, 137.0, 134.5, 127.8, 122.1, 118.7, 118.2, 118.1, 74.0, 73.3.

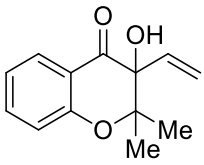
LRMS (ESI) Calcd. for $C_{11}H_{10}O_3$ $[M+Na]^+$: 213, Found: 213.

FTIR (neat): 3454, 2872, 1692.


1.02
1.06
1.07
1.04
1.00
1.04
1.06
1.00
1.07
1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3-Hydroxy-2,2-dimethyl-3-vinylchroman-4-one (2.5e).



The reaction was conducted with 500 mol% of vinyl pivalate at 140 ^{o}C for a 40 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 1% EtOAc/hexanes to 2% EtOAc/hexanes) provided the title compound (57.0 mg, 87%) as a pale yellow oil.

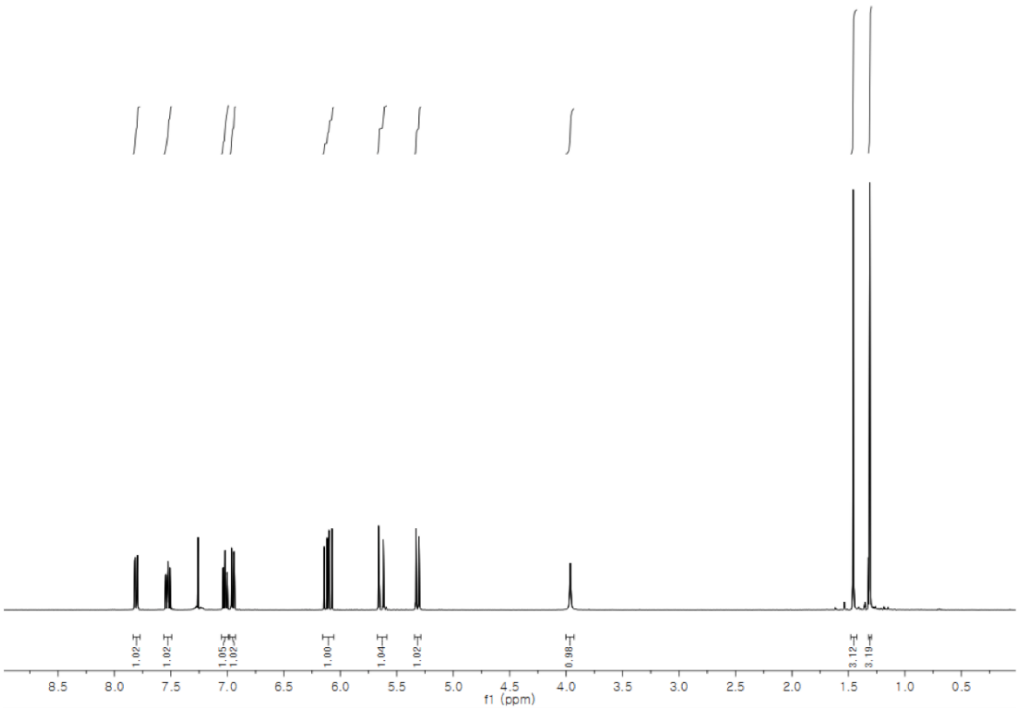
R_f: 0.72 (EtOAc:hexanes = 1:4).

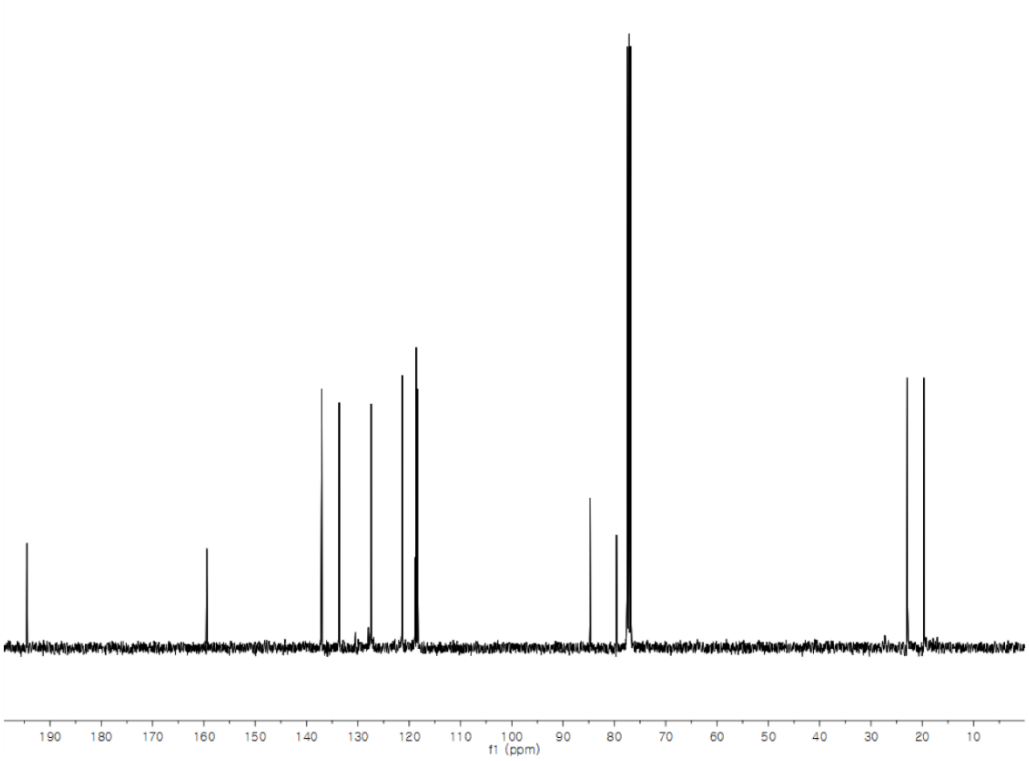
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (ddd, *J* = 7.8 Hz, 1.8 Hz, 0.4 Hz 1H), 7.53 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.8 Hz, 1H), 7.02 (ddd, *J* = 7.8 Hz, 7.2 Hz, 1.0 Hz, 1H), 6.95 (ddd, *J* = 8.4 Hz, 1.0 Hz, 0.4 H,z 1H), 6.11 (dd, *J* = 17.0 Hz, 10.6 Hz, 1H), 5.64 (dd, *J* = 17.0 Hz, 1.5 Hz, 1H), 5.31 (dd, *J* = 10.6 Hz, 1.5 Hz, 1H), 3.96 (s, 1H), 1.46 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 159.5, 137.1, 133.6, 127.4, 121.4, 118.8, 118.6, 118.3, 84.7, 79.6, 22.9, 19.7.

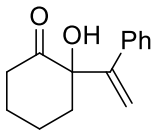
LRMS (CI) Calcd. for $C_{13}H_{14}O_3$ $[M+H]^+$: 219, Found: 219.

FTIR (neat): 3474, 1692.


1.02
1.02
1.05
1.02
1.00
1.04
1.02
0.98
3.12
3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-Hydroxy-2-(1-phenylvinyl)cyclohexan-1-one (2.5f).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-phenylvinyl 2,2,2-triphenylacetate at 150 °C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 35% DCM/hexanes to 65% DCM/hexanes, followed by 5% EtOAc/hexanes) provided the title compound (17.3 mg, 40%) as a pale yellow oil.

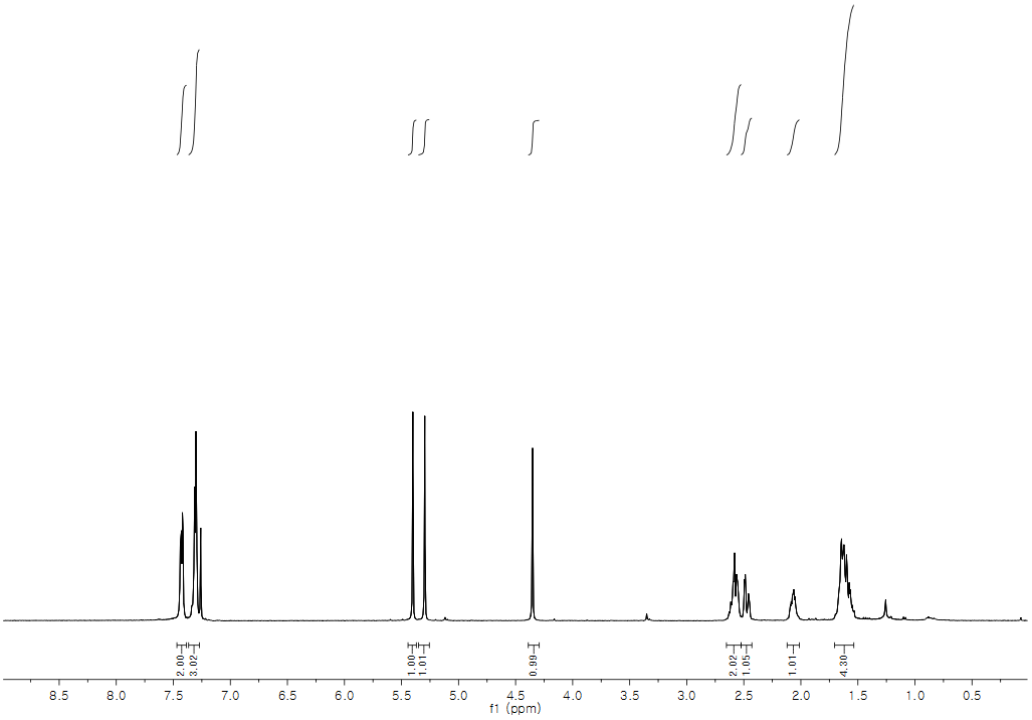
R_f: 0.43 (EtOAc:hexanes = 1:4).

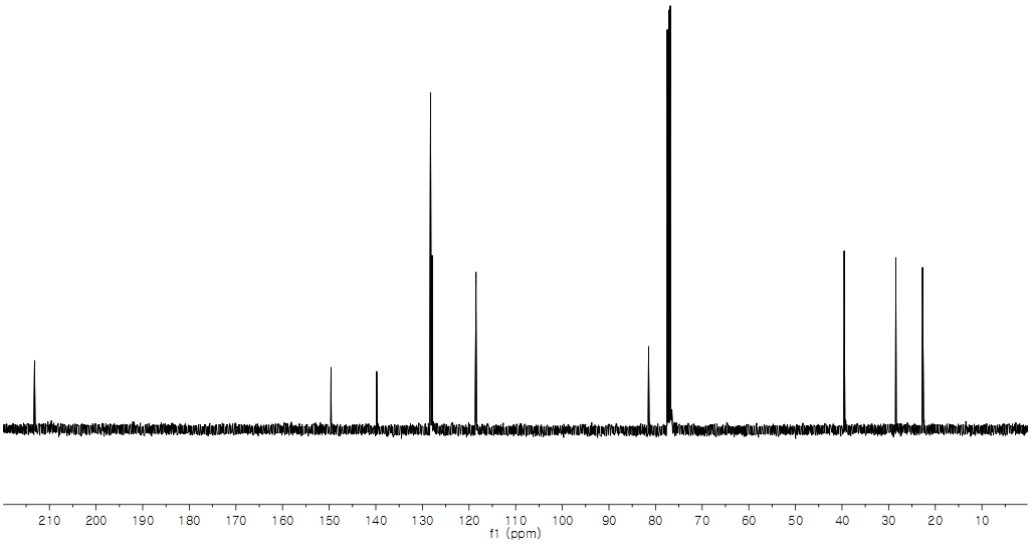
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 6.5 Hz, 3.1 Hz, 2H), 7.37–7.27 (m, 3H), 5.40 (s, 1H), 5.30 (s, 1H), 4.35 (s, 1H), 2.59 (dt, *J* = 9.1 Hz, 6.0 Hz, 2H), 2.52–2.43 (m, 1H), 2.12–2.01 (m, 1H), 1.70–1.54 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 149.6, 139.8, 128.4, 128.3, 127.9, 118.5, 81.5, 39.52, 39.48, 28.5, 22.7.

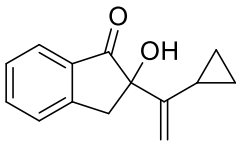
LRMS (ESI) Calcd. for $C_{14}H_{16}O_2$ $[M+Na]^+$: 239, Found: 239.

FTIR (neat): 3470, 2942, 1709.


2.00
3.02
1.00
1.01
0.99
2.02
1.05
1.01
4.30
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-(1-Cyclopropylvinyl)-2-hydroxy-2,3-dihydro-*1H*-inden-1-one (2.6a).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-cyclopropylvinyl 2,2,2-triphenylacetate at 140 ^{o}C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 2% EtOAc/hexanes to 10% EtOAc/hexanes) provided the title compound (30.5 mg, 71%) as a pale yellow oil.

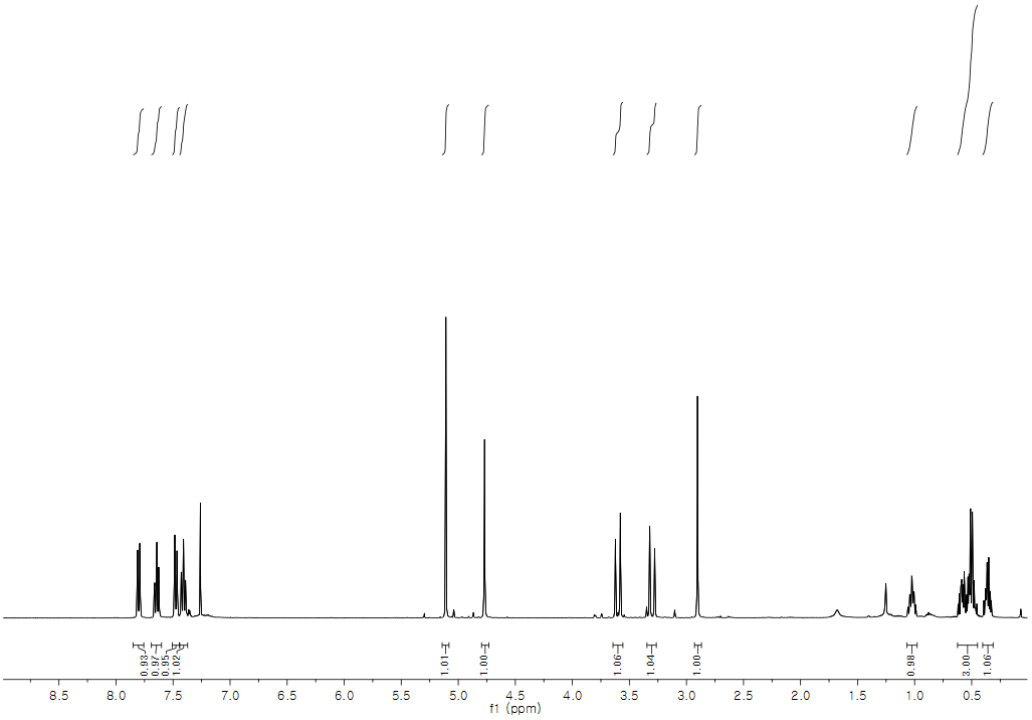
R_f: 0.33 (EtOAc:hexanes = 1:4).

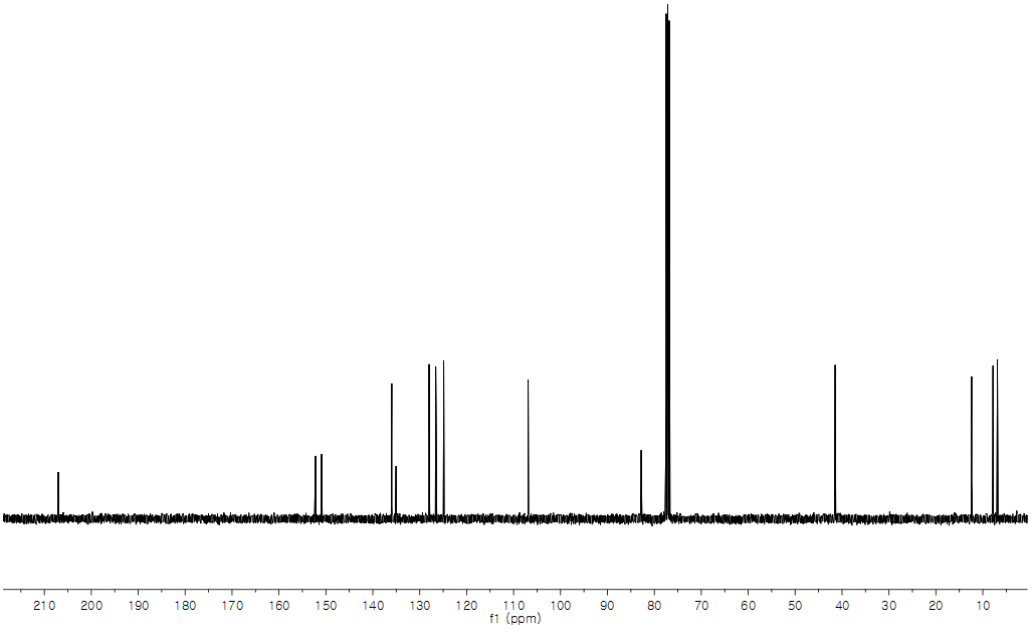
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.64 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.1 Hz, 1H), 7.48 (d, 7.7 Hz, 1H), 7.41 (dd, *J* = 11.1 Hz, 3.9 Hz, 1H), 5.11 (s, 1H), 4.77 (d, *J* = 0.9 Hz, 1H), 3.60 (d, *J* = 17.3 Hz, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 2.90 (s, 1H), 1.07–0.98 (m, 1H), 0.62–0.45 (m, 3H), 0.40–0.31 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.0, 152.2, 150.9, 136.0, 135.0, 128.0, 126.6, 124.9, 106.9, 82.8, 41.5, 12.4, 7.8, 6.9.

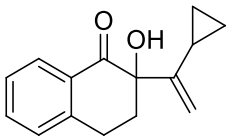
LRMS (CI) Calcd. for $C_{14}H_{14}O_2$ $[M+H]^+$: 215, Found: 215

FTIR (neat): 3444, 3005, 1712.


0.93
0.97
0.95
1.02
1.01
1.00
1.06
1.04
1.00
0.98
3.00
1.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-(1-Cyclopropylvinyl)-2-hydroxy-3,4-dihydronaphthalen-1(*2H*)-one (2.6b).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-cyclopropylvinyl 2,2,2-triphenylacetate at 140 ^{o}C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 35% DCM/hexanes to 70% DCM/hexanes, followed by 5% EtOAc/hexanes) provided the title compound (31.9 mg, 70%) as a pale yellow oil.

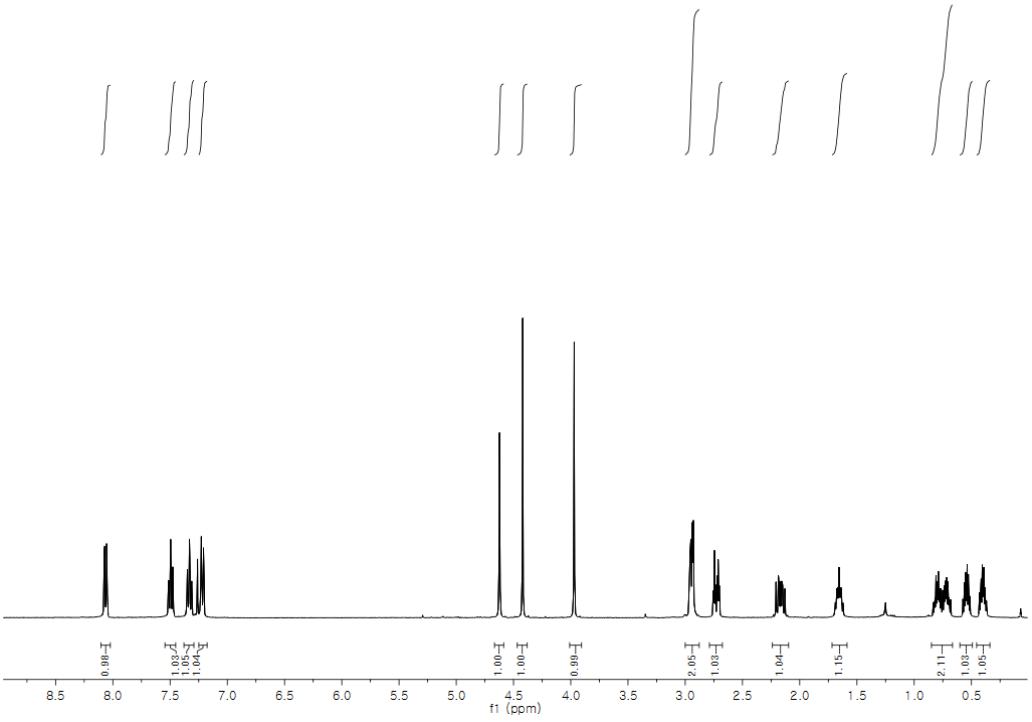
R_f: 0.48 (EtOAc:hexanes = 1:4).

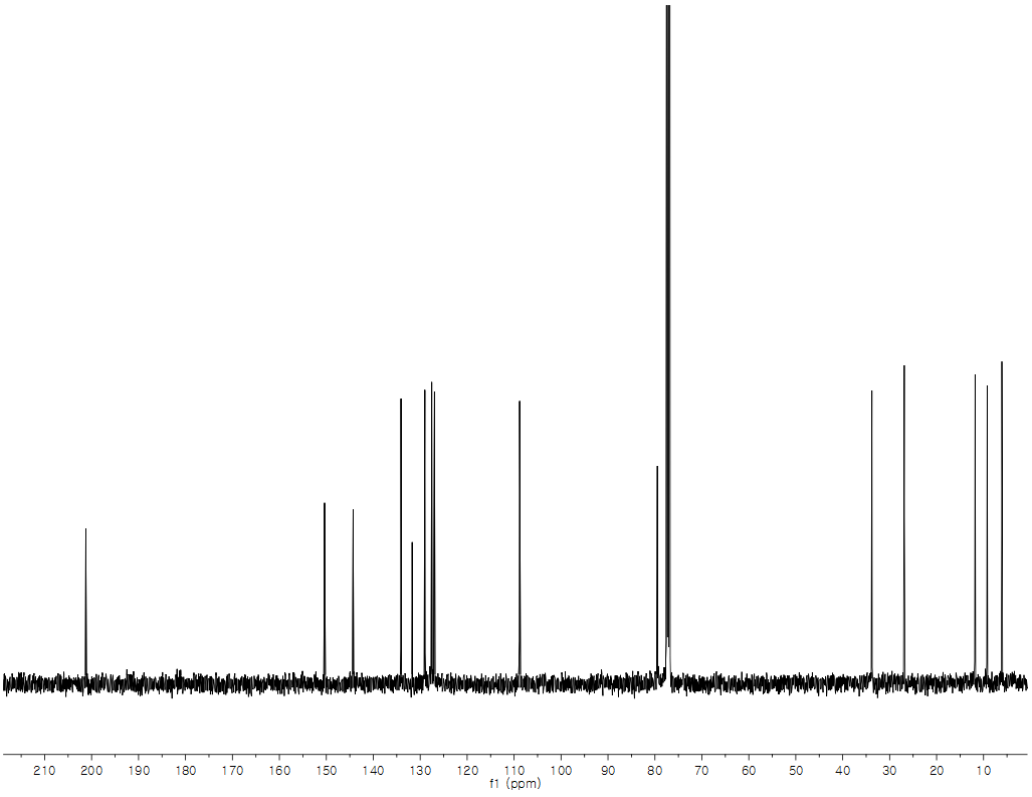
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.49 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 0.7 Hz, 1H), 4.42 (s, 1H), 3.97 (s, 1H), 3.00–2.88 (m, 2H), 2.73 (dt, *J* = 13.3 Hz, 3.7 Hz, 1H), 2.17 (ddd, *J* = 13.4 Hz, 9.7 Hz, 7.9 Hz, 1H), 1.72–1.59 (m, 1H), 0.85–0.67 (m, 2H), 0.54 (ddd, *J* = 9.9 Hz, 7.6 Hz, 5.0 Hz, 1H), 0.40 (dtd, *J* = 9.3 Hz, 5.6 Hz, 3.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 150.4, 144.3, 134.1, 131.7, 129.0, 127.5, 127.0, 108.8, 79.5, 33.8, 26.9, 11.8, 9.2, 6.1.

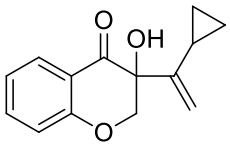
LRMS (CI) Calcd. for $C_{15}H_{16}O_2$ $[M+H]^+$: 229, Found: 229.

FTIR (neat): 3483, 3005, 1683.


0.98
1.02
1.05
1.04
1.00
1.00
0.99
2.05
1.03
1.04
1.15
2.11
1.03
1.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

3-(1-Cyclopropylvinyl)-3-hydroxychroman-4-one (2.6d).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-cyclopropylvinyl 2,2,2-triphenylacetate at 140 °C for a 48 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 35% DCM/hexanes to 80% DCM/hexanes) provided the title compound (41.0 mg, 93%) as a white solid.

R_f: 0.50 (EtOAc:hexanes = 1:4).

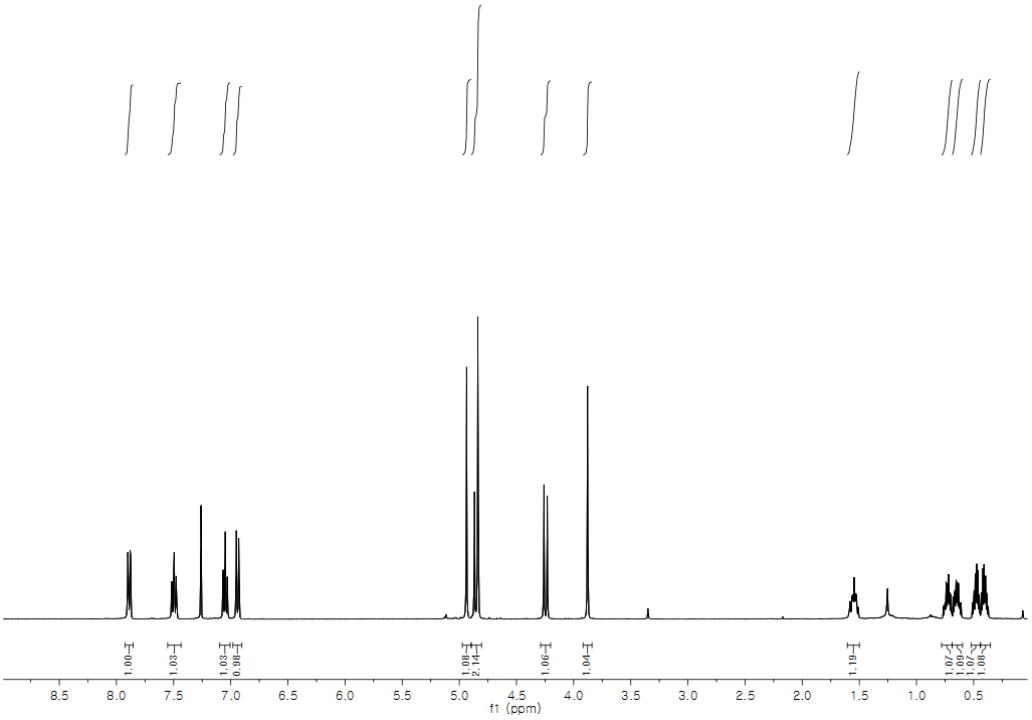
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.7 Hz, 7.3 Hz, 1.7 Hz, 1H), 7.10–7.01 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.94 (s, 1H), 4.85 (d, *J* = 11.6 Hz, 2H), 4.24 (d, *J* = 11.6 Hz, 1H), 3.88 (s, 1H), 1.61–1.50 (m, 1H), 0.73 (tdd, *J* = 8.9 Hz, 5.6 Hz, 3.7 Hz, 1H), 0.69–0.60 (m, 1H), 0.52–0.44 (m, 1H), 0.41 (ddd, *J* = 13.4 Hz, 7.5 Hz, 4.7 Hz, 1H)

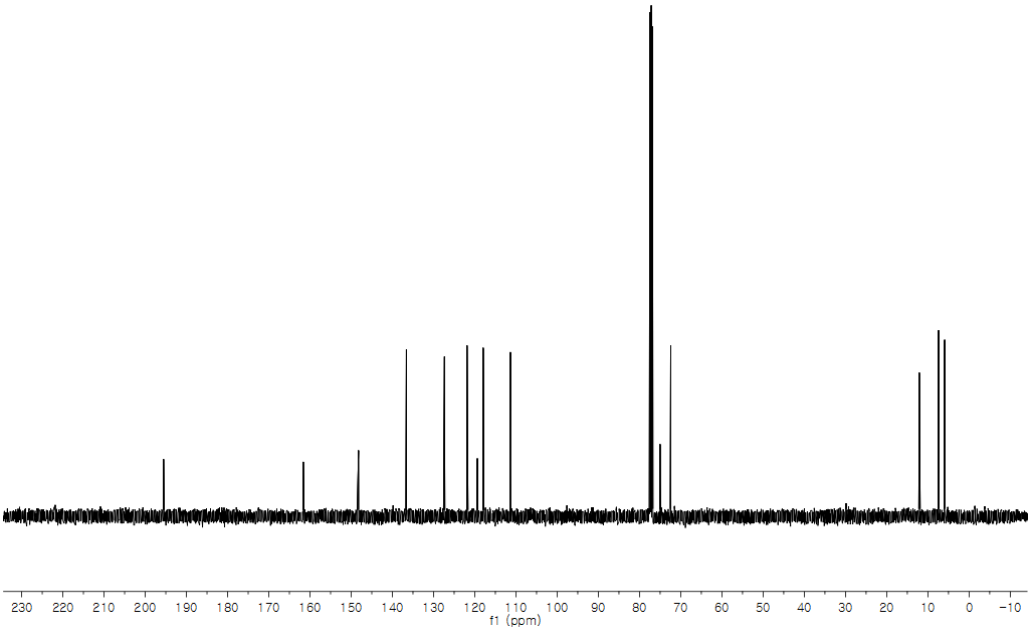
^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 161.6, 148.2, 136.6, 127.4, 121.9, 119.4, 118.0, 111.4, 75.0, 72.4, 12.1, 7.4, 5.9.

LRMS (ESI) Calcd. for $C_{14}H_{14}O_3$ $[M+Na]^+$: 253, Found: 253

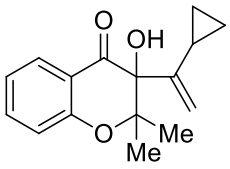
FTIR (neat): 3450, 3006, 1692.

MP: 59 °C


1.00
1.03
1.03
0.98
1.08
2.14
1.06
1.04
1.19
1.07
1.09
1.07
1.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3-(1-Cyclopropylvinyl)-3-hydroxy-2,2-dimethylchroman-4-one (2.6e).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-cyclopropylvinyl 2,2,2-triphenylacetate at 150 ^{o}C for a 40 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 20% DCM/hexanes, followed by 1.5% Ether/hexanes) provided the title compound (42.4 mg, 82%) as a pale yellow oil.

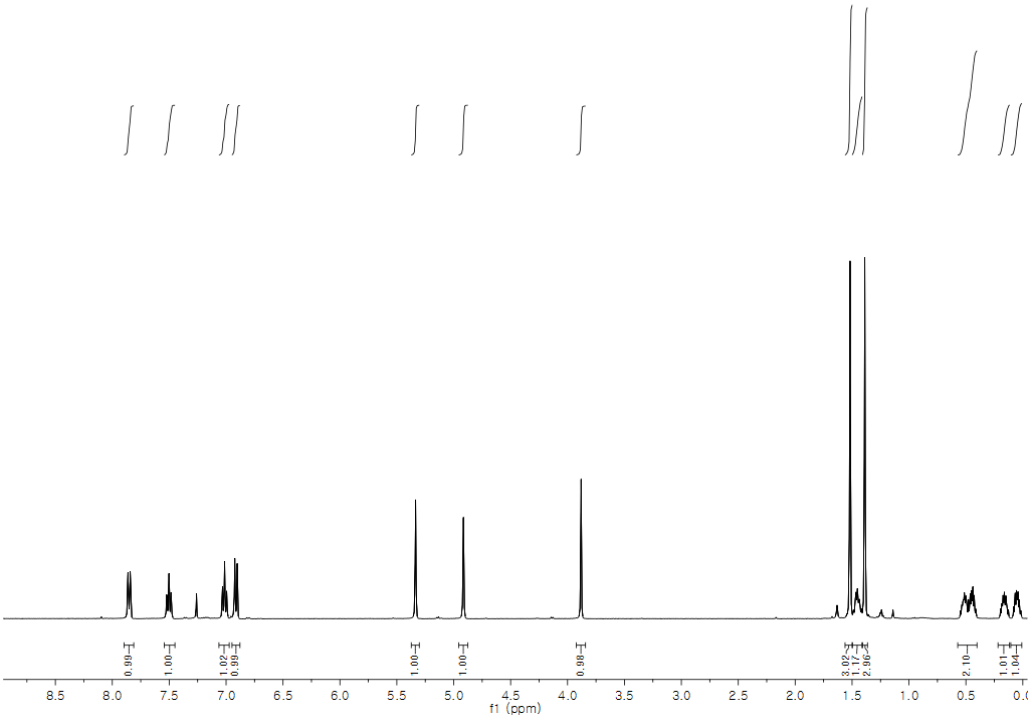
R_f: 0.75 (EtOAc:hexanes = 1:4).

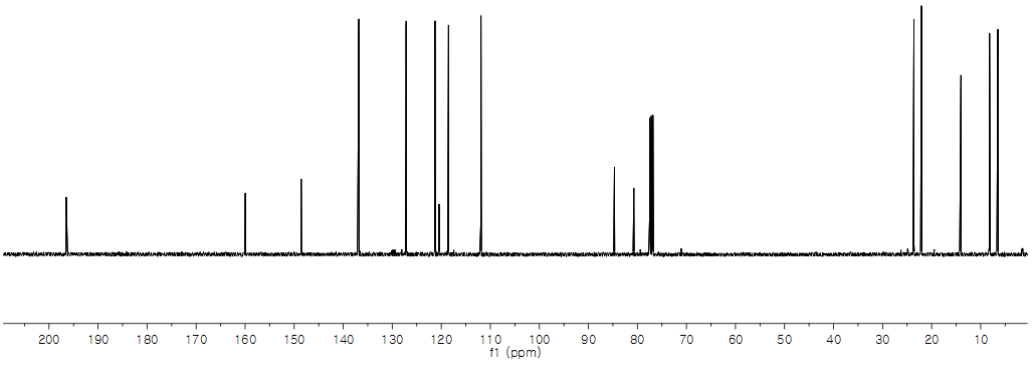
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.54–7.45 (m, 1H), 7.01 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.33 (s, 1H), 4.91 (s, 1H), 3.88 (s, 1H), 1.52 (s, 3H), 1.50–1.41 (m, 1H), 1.39 (s, 3H), 0.57–0.40 (m, 2H), 0.16 (ddd, *J* = 14.9 Hz, 9.0 Hz, 5.1 Hz, 1H), 0.05 (dt, *J* = 9.8 Hz, 5.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 160.0, 148.6, 136.8, 127.2, 121.3, 120.5, 118.5, 111.9, 84.7, 80.7, 23.6, 22.1, 14.0, 8.2, 6.5.

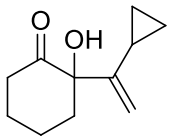
LRMS (CI) Calcd. for $C_{16}H_{18}O_3$ $[M+H]^+$: 259, Found: 259.

FTIR (neat): 3481, 3001, 1686.


0.99
1.00
1.02
0.99
1.00
1.00
0.98
3.02
1.17
2.96
2.10
1.01
1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-(1-Cyclopropylvinyl)-2-hydroxycyclohexanone (2.6f).



The reaction (0.2 mmol scale) was conducted with 500 mol% of 1-cyclopropylvinyl 2,2,2-triphenylacetate at 150 ^{o}C for a 24 hour period in accordance with the general procedure. Flash column chromatography (SiO_2, 30% DCM/hexanes to 65% DCM/hexanes followed by 5% EtOAc:hexanes) provided the title compound (35.1 mg, 65%) as a pale yellow oil.

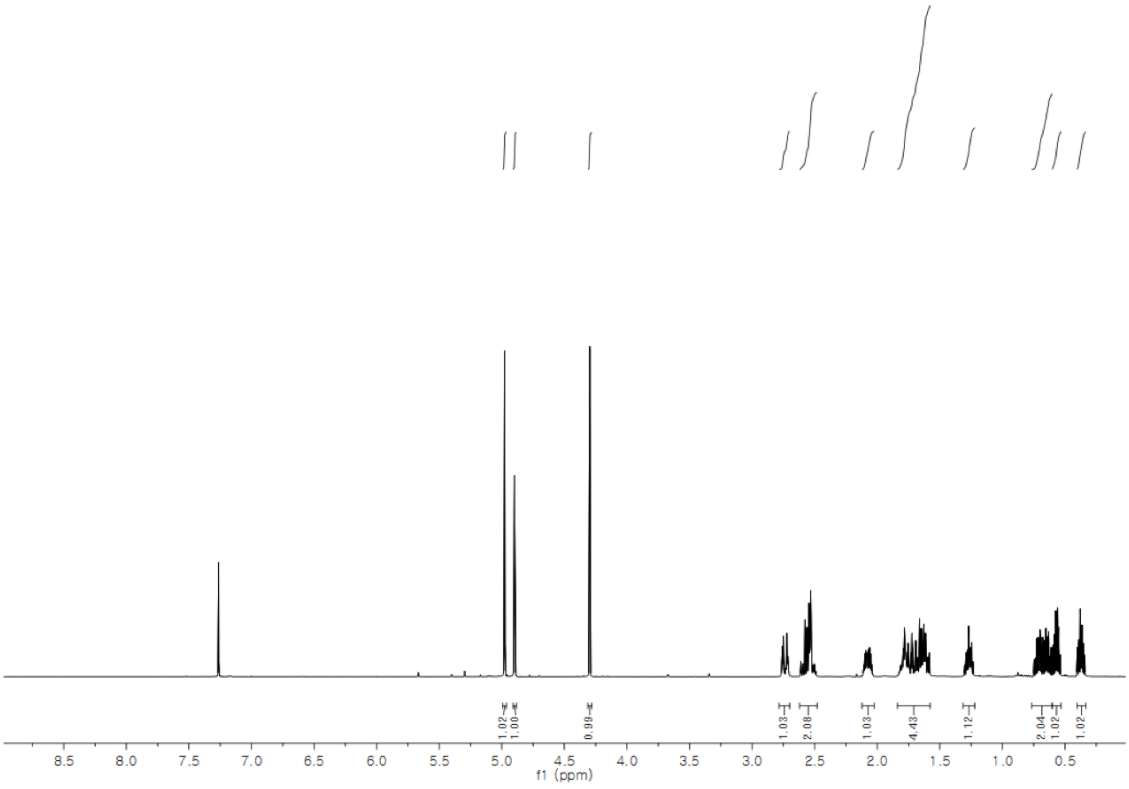
R_f: 0.39 (EtOAc:hexanes = 1:4).

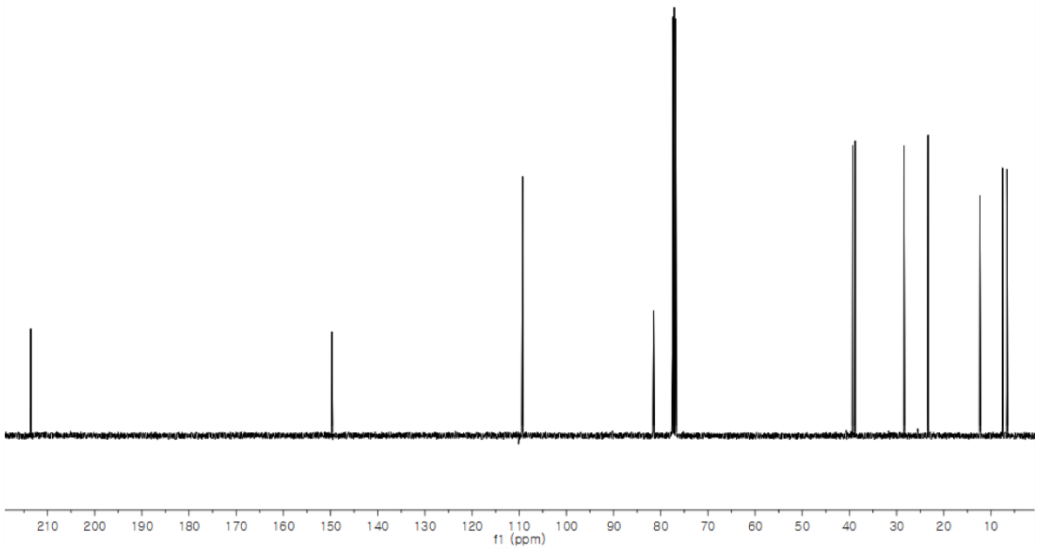
^{1}H NMR (400 MHz, $CDCl_3$): 4.98 (s, 1H), 4.90 (d, *J* = 1.1 Hz, 1H), 4.30 (s, 1H), 2.74 (dq, *J* = 13.6 Hz, 2.9 Hz, 1H), 2.62–2.48 (m, 2H), 2.12–2.02 (m, 1H), 1.84–1.58 (m, 4H), 1.27 (ttd, *J* = 8.3 Hz, 5.4 Hz, 1.1 Hz, 1H), 0.77–0.60 (m, 2H), 0.57 (dtd, *J* = 9.2 Hz, 5.5 Hz, 3.7 Hz, 1H), 0.40–0.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.5, 149.7, 109.3, 81.5, 39.3, 38.8, 28.4, 23.3, 12.4, 7.6, 6.6.

LRMS (CI) Calcd. for $C_{11}H_{16}O_2$ $[M+H]^+$ and $[M-OH]^+$: 181 and 163, Found: 181 and 163.

FTIR (neat): 3466, 2943, 1710.


1.02
1.00
0.99
1.03
2.08
1.03
4.43
1.12
2.04
1.02
1.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Chapter 3: Osmium(0)-Catalyzed C−C Coupling of Ethylene and α-Olefins with Diols, Ketols, or Hydroxy Esters via Transfer Hydrogenation*

3.1 Introduction

While α-olefins are the most abundant petrochemical feedstock,[1] the use of α-olefins in the commercial manufacture of commodity chemicals is limited to polymerization,[2] hydroformylation[3] and alkene metathesis.[4] The discovery of alternate catalytic C-C couplings methodology which convert α-olefins to value-added products remain elusive. For example, while intermolecular alkene hydroacylation is attractive, decarbonylation of acylmetal intermediates to form inactive metal carbonyl complexes mandates use of uncommon reactants bearing chelating groups.[5,6] Similarly, intermolecular Prins or carbonyl ene reactions are not readily applicable to the coupling of α-olefins and ketones.[7a-c] Finally, whereas nickel(0) catalyzes the coupling of α-olefins with simple aldehydes, superstoichiometric quantities of TESOTf and Et_3N are required.[7d] During the course of the development of transfer hydrogenative C-C bond forming reactions,[8] we recently found that zero-valent ruthenium complexes generated *in situ* from $Ru_3(CO)_{12}$ modified with phosphine ligands were able to catalyze the C-C coupling of vicinally dioxygenated hydrocarbons (1,2-diols, α-ketols, α-hydroxy esters) with a range of π-unsaturated reactants, including dienes,[9a-d] acrylates[9e] and alkynes.[9g,h,j] As in related ruthenium(0) catalyzed Pauson-Khand reactions of vicinal dicarbonyl compounds illustrated by Chatani and Murai,[10] these reactions are initiated from oxidative cyclometallation with carbonyl and unsaturated coupling

* This chapter is based on the published work:
Park, B. Y.; Luong, T.; Sato, H.; Krische, M. J. *J. Org. Chem.* **2016**, *81*, 8585.
Contribution of HS: A few substrate scope of ethyl mandate and a few substrate scope of diol and one of α-olefin substrate scope were done by HS.

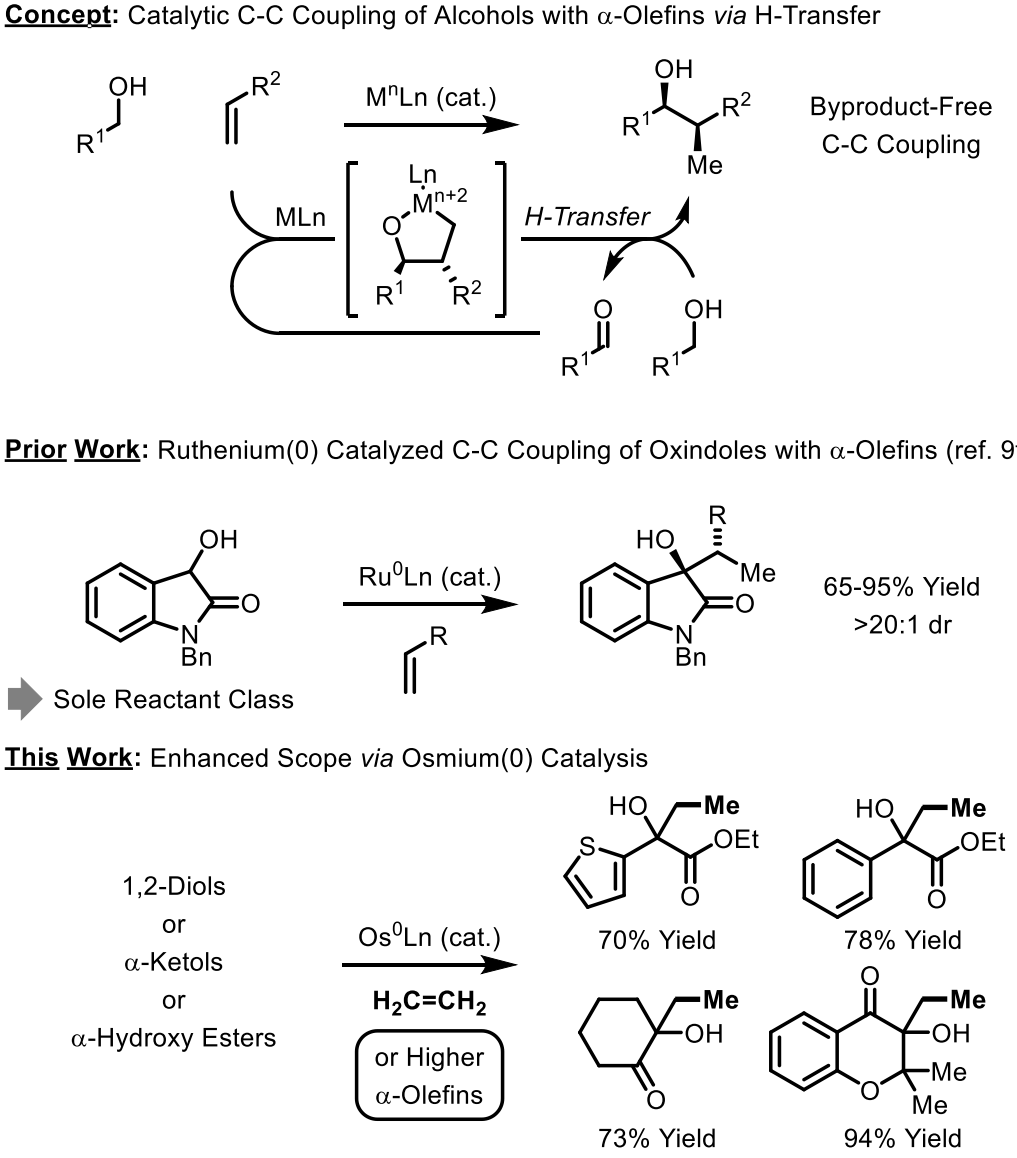


Figure 3.1. General mechanism for catalytic C-C coupling of alcohols with π-unsaturated reactants via hydrogen auto-transfer and applications toward the coupling of α-olefins.

partners to furnish oxaruthenacycles. Following hydrogen transfer from the alcohol reactant to the oxo-ruthenacycle releases the desired product and regenerates the carbonyl partner (Figure 3.1, top). Based on this mechanism, a ruthenium(0) catalyzed coupling of α-olefins was developed (Figure 3.1, middle).[9f] This reaction, however, was limited to 3-hydroxy-2-oxindoles as coupling partners. Herein, we will show that the advent of osmium(0) catalysts modified by phosphine

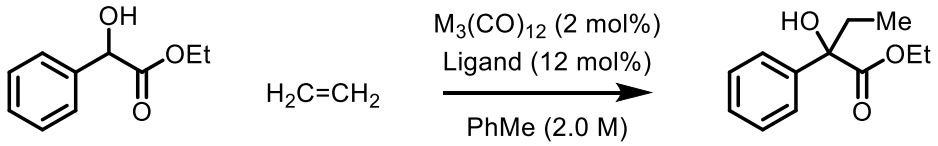
ligands improve the reaction scope, enabling the direct C-C coupling of ethylene[11] and other simple α-olefins with diverse diols, α-ketols and α-hydroxy esters (Figure 3.1, bottom).

3.2 Research Design and Method

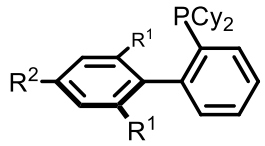
Presumably, the scope limitation of ruthenium(0) catalyzed C-C couplings of α-olefins[9f] is caused by a high energetic barrier to oxidative coupling. Based on Hoffmann's theoretical analysis of the conversion of metal bisolefin complexes to metalacyclopentanes,[12] and a large body of experimental evidence,[13a] the ability of oxidative coupling should be dependent on the strength of backbonding in metal-olefin π-complexes.[14] π-Backbonding gives nucleophilic character to the olefin bounded to the metal, and in some cases, may be viewed as an oxidative addition to the C=C π-bond to form a metalacyclopropane. For example, the Kulinkovich reaction,[15] wherein titanium(II)-olefin complexes behave as vicinal dianions, is a representative example of this effect. Thus, introduction of a more strongly reducing metal center should promote oxidative cyclometallation to expand the substrate scope in transfer hydrogenative C-C couplings of α-olefins.

As a comparison between ruthenium and osmium carbonyl complexes $HClM(CO)(PPh_3)_3$, M = Os, ν_{co} = 1906 cm^{-1}; M = Ru, ν_{co} = 1922 cm^{-1}, osmium is a stronger π-donor than ruthenium.[16] Based on the hypothesis mentioned above, osmium should facilitate oxidative cyclometallation and expand the scope. In fact, a range of activated secondary alcohols are used as coupling partner with osmium(0) catalysts in previously reported vinyl transfer reactions.[9i] For this reason, osmium(0) complexes were examined for C-C couplings of α-olefins. The reactions of ethyl mandelate **3.1a** with ethylene **3.2a** were investigated with osmium catalysts aiming for the ethylated tertiary alcohol **3.3a** (Scheme 3.1). Monodentate or bidentate triaryl phosphine ligands

failed. To our delight, the osmium(0) catalyst modified by PCy_3 (tricyclohexylphosphine) provided the desired ethylated alcohol in 57% yield. After screening, the osmium(0) complex modified by XPhos was deemed as the optimal catalyst. Intriguingly, the corresponding ruthenium(0) carbonyl catalysts did not afford the desired ethylated alcohol **3.3a**.



3.1a (100 mol%) **3.2a** (1 atm) **3.3a**



RuPhos, R^1 = O-^{i}Pr, R^2 = H
XPhos, R^1 = R^2 = ^{i}Pr
CyJohnPhos, R^1 = R^2 = H

Metal	Ligand	Yield
Ru	PCy_3	---
Os	PCy_3	57
Ru	CyJohnPhos	---
Os	CyJohnPhos	31
Ru	RuPhos	---
Os	RuPhos	60
Ru	XPhos	---
Os	**XPhos**	**78**

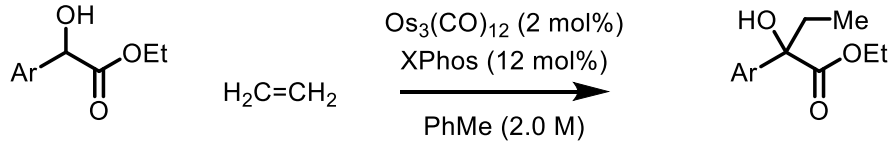
Scheme 3.1. Selected experiments in the coupling of ethyl mandelate **3.1a** with ethylene **3.2a** to form tertiary alcohol **3.3a**.[a]

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details

3.3 Results and Discussion

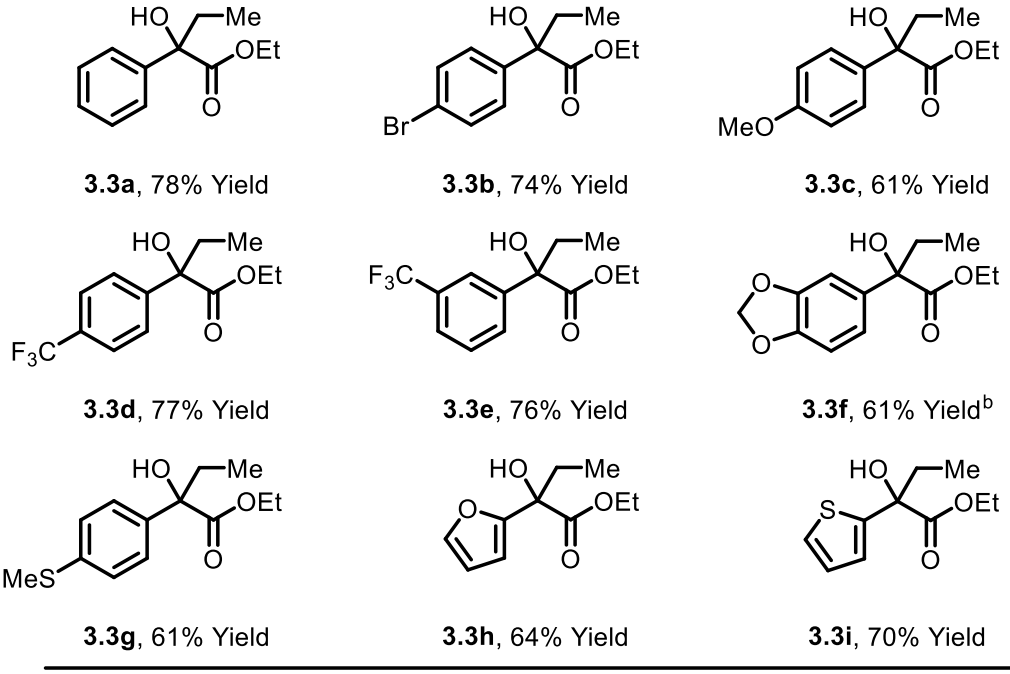
Under these optimal conditions, the reaction of aryl- and heteroaryl-substituted α-hydroxy esters **3.1a**-**3.1i** and ethylene **3.2a** gave the products of carbinol C-H ethylation **3.3a**-**3.3i** (Table 3.1). As illustrated by the conversion of ethyl 4-bromomandelate **3.1b** to adduct **3.3b**, aryl halide functional groups are tolerated. Both the electron rich substrate 4-methoxymandelate **3.1c** and electron deficient substrate ethyl 4-(trifluoromethyl)mandelate **3.1d** give the desired products **3.3c** and **3.3d** respectively. Substituents at the *meta*-position of the aryl ring are tolerated, as shown in

Table 3.1. Osmium(0) catalyzed coupling of α-hydroxy esters **3.1a-3.1i** with ethylene **3.2a** to form tertiary alcohols **3.3a-3.3i**.[a]



3.1a-i (100 mol%) | **3.2a** (1 atm) | 130 °C | **3.3a-i**

3.1a, Ar = Ph	**3.1b**, Ar = 4-Br-Ph	**3.1c**, Ar = 4-MeO-Ph
3.1d, Ar = 4-CF_3-Ph	**3.1e**, Ar = 3-CF_3-Ph	**3.1f**, Ar = 5-(benzodioxole)
3.1g, Ar = 4-MeS-Ph	**3.1h**, Ar = 2-furyl	**3.1i**, Ar = 2-thienyl



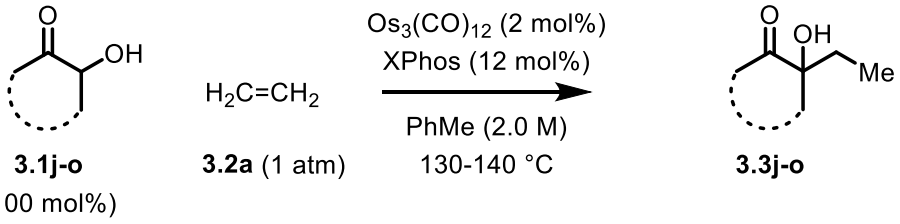
3.3a, 78% Yield	**3.3b**, 74% Yield	**3.3c**, 61% Yield
3.3d, 77% Yield	**3.3e**, 76% Yield	**3.3f**, 61% Yield[b]
3.3g, 61% Yield	**3.3h**, 64% Yield	**3.3i**, 70% Yield

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]140 °C.

the formation of **3.3e** and **3.3f**, respectively. Finally, sulfur containing α-hydroxy ester **3.1g** and heteroaromatic α-hydroxy esters **3.1h** and **3.1i** groups are converted to adducts **3.3g**, **3.3h** and **3.3i**, respectively. *ortho*-Substituted mandelates and alkyl-substituted α-hydroxy esters such as ethyl lactate, were inefficient.

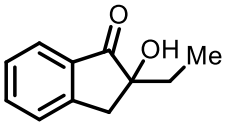
Next α-ketols, which can form 1,2-diketones as reactive intermediates, were explored. Under optimal conditions the reactions of α-ketols **3.1j-3.1o** with ethylene **3.2a** delivered the

Table 3.2. Osmium(0) catalyzed coupling of α-ketols **3.1j-3.1o** with ethylene **3.2a** to form tertiary alcohols **3.3j-3.3o**.[a]

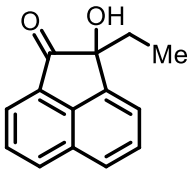


3.1j-o (100 mol%) **3.2a** (1 atm) **3.3j-o**

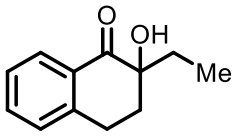
3.1j, 2-OH-indanone **3.1k**, 2-OH-acenaphthylenone **3.1l**, 2-OH-tetralone
3.1m, 3-OH-chromanone **3.1n**, 3-OH-2,2-Me_2-chromanone **3.1o**, 2-OH-cyclohexanone



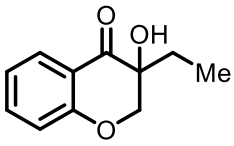
3.3j, 84% Yield



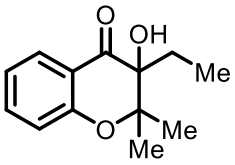
3.3k, 63% Yield



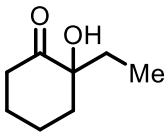
3.3l, 83% Yield[b]



3.3m, 86% Yield



3.3n, 85% Yield

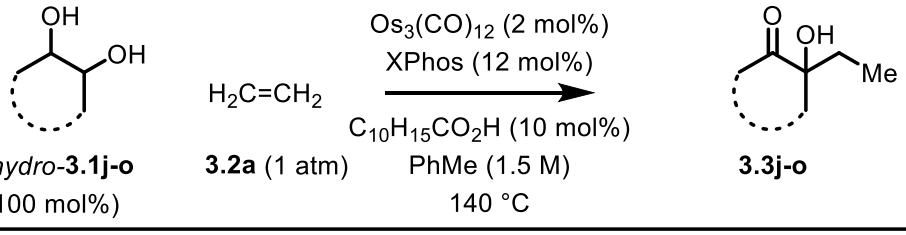


3.3o, 73% Yield

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]C10H15CO2H (10 mol%)

ethylated tertiary alcohols **3.3j-3.3o** in good to excellent yield (Table 3.2). Furthermore, in the coupling of α-ketols **3.1j**, **3.1l-3.1n**, which proceed by way of unsymmetric 1,2-diketones, the adducts **3.3j**, **3.3l-3.3n** were obtained as single regioisomers. The effect of electronic effects in the event of oxidative coupling as described by Hoffman[12] and in prior work from our laboratory,[9e] as well as steric effects are crucial to regioselectivity. That is, oxidative coupling will occur wherein the osmium center causes less steric demand. α-Ketol **3.1n** is an exception due to the electronic effect associated with the mesomeric effect of the *ortho*-oxygen atom.

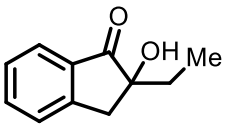
Table 3.3. Osmium(0) catalyzed coupling of 1,2-diols dihy-dro-**3.1j**-**3.1o** with ethylene **3.2a** to form tertiary alcohols **3.3j**-**3.3o**.[a]



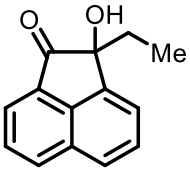
dihydro-**3.1j-o** (100 mol%) | **3.2a** (1 atm) | **3.3j-o**

H_2-**3.1j**, indane diol | H_2-**3.1k**, acenaphthylene diol | H_2-**3.1l**, H_4-naphthalene diol

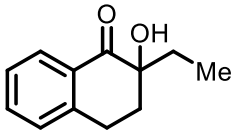
H_2-**3.1m**, chromane diol | H_2-**3.1n**, 2,2-Me_2-chromane diol | H_2-**3.1o**, cyclohexane diol



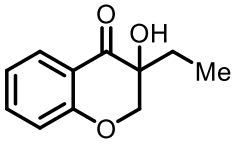
3.3j, 71% Yield



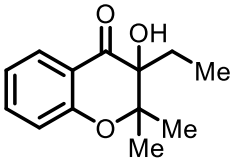
3.3k, 70% Yield



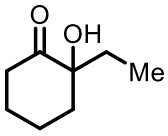
3.3l, 71% Yield



3.3m, 60% Yield



3.3n, 94% Yield

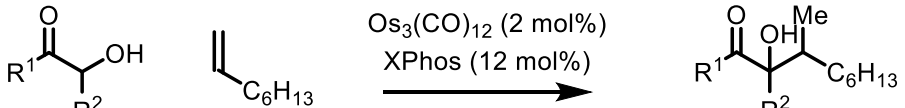


3.3o, 50% Yield[b]

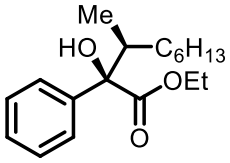
[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]Reaction conducted in mesitylene at 150 °C using $Os_3(CO)_{12}$ (3 mol%), XPhos (18 mol%), $C_{10}H_{15}CO2H$ (15 mol%).

The coupling of ethylene **3.2a** with α-hydroxy esters **3.1a**-**3.1i** or α-ketols **3.1j**-**3.1o** to form adducts **3.3a**-**3.3o** are redox-neutral transformations. In contrast, the reactions of ethylene **3.2a** with 1,2-diols *dihydro*-**3.1j**-**3.1o** are oxidative processes in which one equivalent of sacrificial hydrogen acceptor is necessary (Table 3.3). There are many reports that transfer hydrogenation undergoes with ruthenium catalysts, for example Shvo, who demonstrates that zero-valent ruthenium catalysts derived from $Ru_3(CO)_{12}$ promote oxidative esterifications in which tolane (diphenyl acetylene) serves as H_2-acceptor,[17] as well as work from our laboratory on oxidative diol-diene [4+2] cycloadditions.[9c] As a ruthenium analogy of the same 8 group transition metal, $Os_3(CO)_{12}$ was examined in the event of ethylation. Initial attempts at the coupling of ethylene

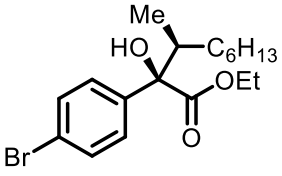
Table 3.4. Osmium(0) catalyzed coupling of **3.1a**, **3.1b**, **3.1i**, **3.1j**, **3.1k**, **3.1m** with 1-octene **3.2b** to form **3.4a**, **3.4b**, **3.4i**, **3.4j**, **3.4k**, **3.4m**.[a]



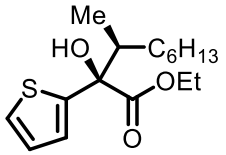
3.1a,**b**,**i**,**j**,**k**,**m** (100 mol%) | **3.2b** (500 mol%) | **3.4a**,**b**,**i**,**j**,**k**,**m**



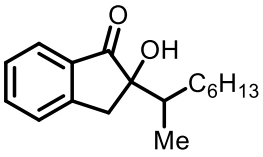
3.4a, 62% Yield
5:1 dr



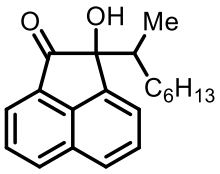
3.4b, 61% Yield
4:1 dr (X-ray)



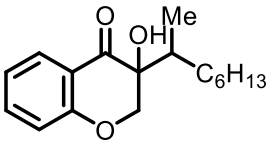
3.4i, 80% Yield
5:1 dr



3.4j, 85% Yield
1:1 dr



3.4k, 95% Yield
2:1 dr



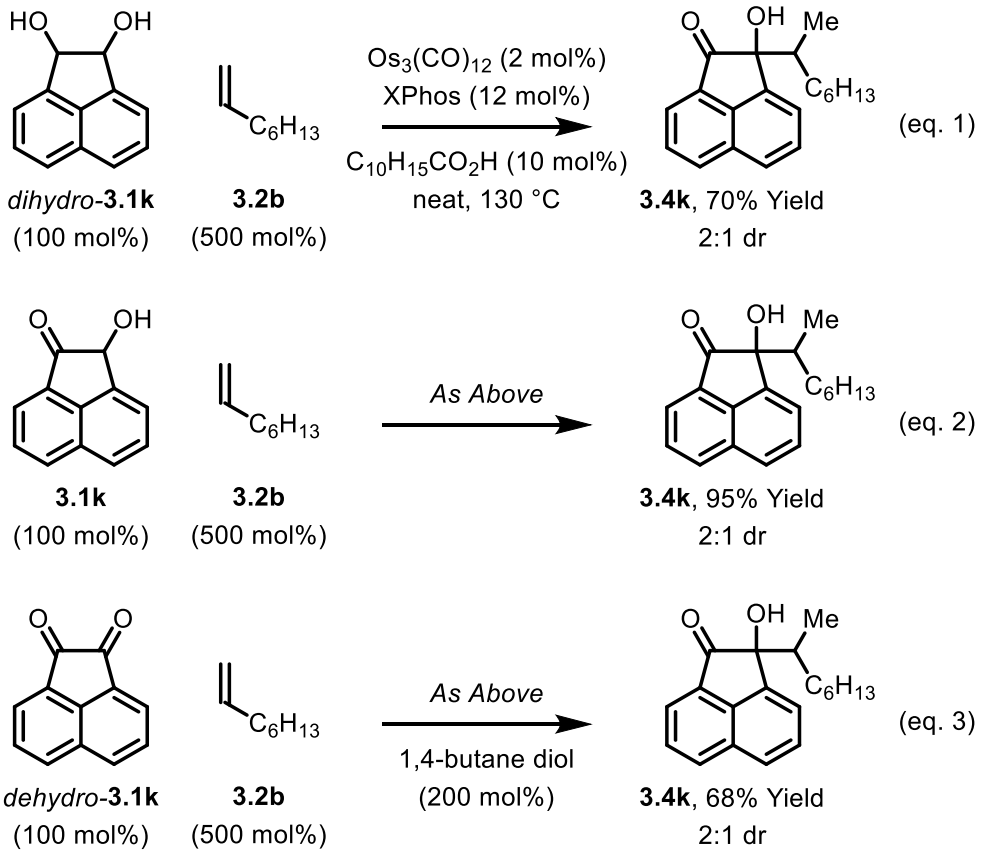
3.4m, 63% Yield
1:1 dr

[a]Yields are of material isolated by silica gel chromatography. See Experimental Section for further experimental details.

3.2a with 1,2-diols *dihydro*-**3.1j**-**3.1o** using the osmium(0) catalyst modified by XPhos led to only modest yields of ethylated adducts **3.3j**-**3.3o**. Expecting carboxylic acids would accelerate the hydrogenolysis[13] and transfer hydrogenolysis[9e] of oxa-metalacycles, these reactions were conducted in the presence of adamantane carboxylic acid (10 mol%). To our delight, the yields of adducts **3.3j**-**3.3o** were remarkably improved.

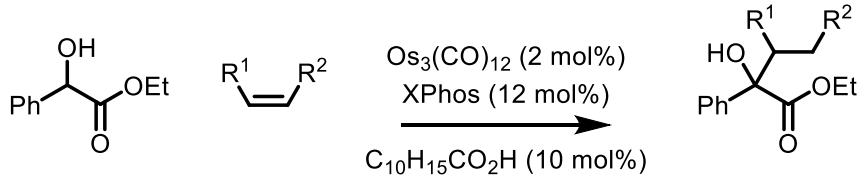
To investigate the generality of these reactions to higher α-olefins, the coupling of 1-octene **3.2b** with α-hydroxy esters **3.1a**, **3.1b** and **3.1i** and α-ketols **3.1j**, **3.1k** and **3.1m** was attempted (Table 3.4). Although corresponding reactions of ethylene **3.2a** proceed efficiently in the absence

of a carboxylic acid cocatalyst, couplings of 1-octene **3.2b** required the presence of adamantane carboxylic acid (10 mol%) to increase conversion. Additionally, higher concentrations were beneficial, so the reactions were conducted neat. The α-hydroxy esters **3.1a**, **3.1b** and **3.1i** were converted to adducts **3.4a**, **3.4b** and **3.4i**, respectively, with complete levels of branched regioselectivity and good levels of diastereoselectivity. Relative stereochemistry for adducts **3.4a**, **3.4b** and **3.4i** was determined by single crystal X-ray diffraction analysis of a derivative of **3.4b**. A stereochemical model is proposed (Scheme 3.3). α-Ketols **3.1j**, **3.1k** and **3.1m** were converted to adducts **3.4j**, **3.4k** and **3.4m** in a completely regioselective manner, but in moderate diastereoselectivity.



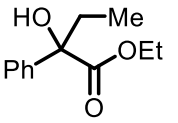
Scheme 3.2 Osmium(0) catalyzed redox independent coupling of 1-octene **3.2b** with *dihydro*-, *dehydro*-**3.1k**.

Table 3.5. Osmium(0) catalyzed coupling of ethyl mandelate 3.1a with functionalized olefins **3.2a-3.2f**.[a]

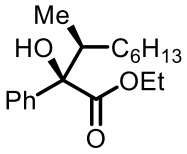


3.1a (100 mol%) | **3.2a-f** (500 mol%) | **3.3a-8a**

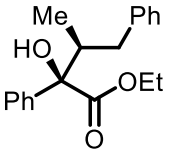
3.2a, $R^1 = R^2 = H$ | **3.2b**, $R^1 = H$, $R^2 = C_6H_{13}$ | **3.2c**, $R^1 = H$, $R^2 = CH_2Ph$
3.2d, $R^1 = H$, $R^2 = OPiv$ | **3.2e**, dihydrofuran | **3.2f**, $R^1 = H$, $R^2 = CH_2OAc$



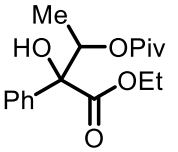
3.3a, 78% Yield[b]



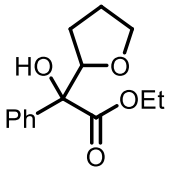
3.4a, 62% Yield[c]
5:1 dr



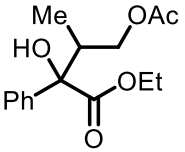
3.5a, 58% Yield[d]
5:1 dr



3.6a, 84% Yield[b,e,f]
1.5:1 dr



3.7a, 78% Yield[b,e,f]
1:1 dr



3.8a, 60% Yield
1.6:1 dr

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]$C_{10}H_{15}CO_2H$ was omitted. [c]Neat. [d]$C_{10}H_{15}CO_2H$ (30 mol%) [e]**3.2d** (300 mol%). [f]XPhos was omitted.

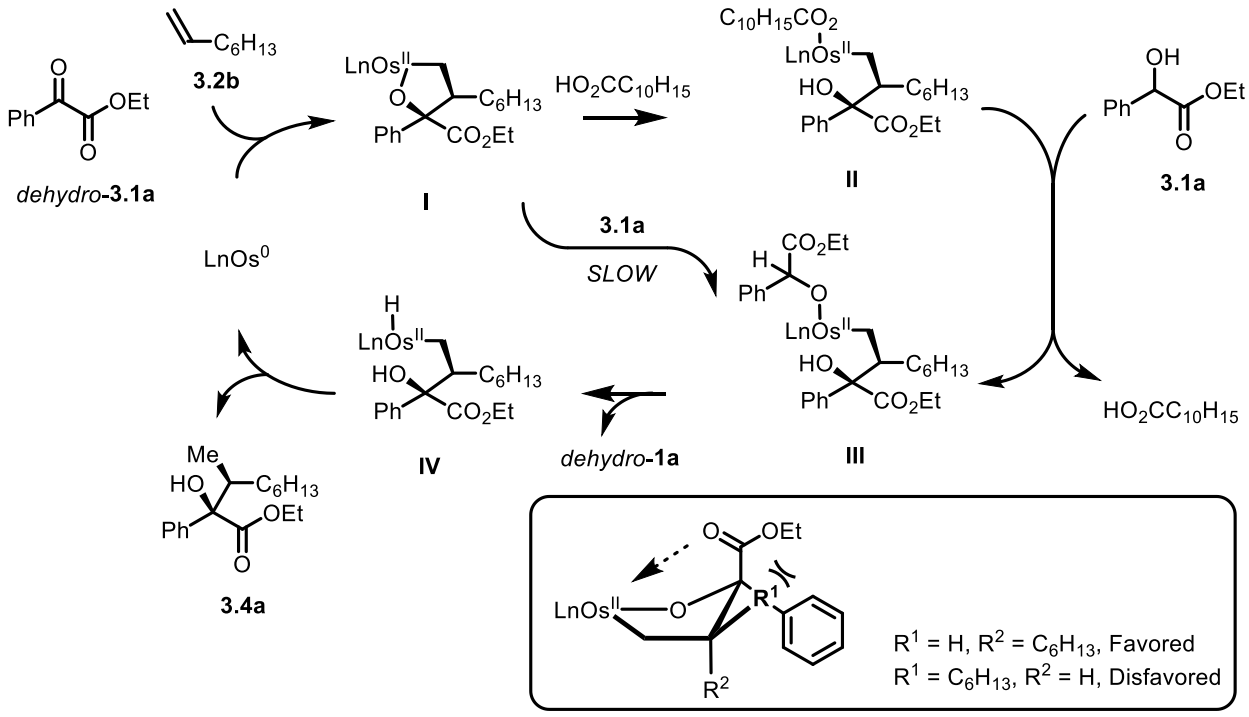
The present transfer hydrogenative couplings of α-olefins can be conducted in either oxidative, redox-neutral or reductive modes. While redox-neutral couplings are most efficient, the alternate of oxidative and reductive transformations are useful to expand substrate scope. The following transformations with redox-variant substrates demonstrates this unique capability (eqs. 1-3). In the oxidative coupling of 1-octene **3.2b** with diol *dihydro*-**3.1k**, wherein 1-octene serves as hydrogen acceptor, adduct **3.4k** forms in 70% yield (Scheme 3.2 eq. 1). The redox-neutral coupling of 1-octene **3.2b** with α-ketol **3.1k** proceeds in 95% yield (Scheme 3.2 eq. 2). Finally, using 1,4-butanediol as terminal reductant,[18] the reductive coupling of 1-octene **3.2b** with the 1,2-

dione *dehydro*-**3.1k** proceeds in 68% yield (Scheme 3.2 eq. 3). Such redox-variable substrate scope allows to bypassing of discrete manipulations for starting substrate preparation otherwise required for the adjustment of oxidation level.[19]

To evaluate the scope of the alkene partner, the coupling of olefins **3.2a**-**3.2f** with ethyl mandelate **3.1a** was explored (Table 3.5). Beyond the couplings of ethylene **3.2a** and 1-octene **3.2b**, allyl benzene **3.2c** undergoes in C-C coupling to give tertiary alcohol **3.5a**. For carboxy- and alkoxy-substituted alkenes **3.2d** and **3.2e**, the indicated regioisomers **3.6a** and **3.7a** are formed exclusively. Here, omission of XPhos and adamantane carboxylic acid is required to suppress metalacycle fragmentation *en route* to products of vinyl transfer (not shown).[9i] Finally, allyl acetate **3.2f** participates in C-C coupling to form adduct **3.8a** with complete levels of branched regioselectivity.

3.4 Mechanism

A plausible mechanism is proposed (Scheme 3.3). It is not clear whether the osmium active catalyst is mononuclear or multinuclear. After heating in toluene solutions of $Os_3(CO)_{12}$ with XPhos in the presence and absence of adamantane carboxylic acid ($AdCO_2H$), crystals of the dinuclear complex $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ and the trinuclear complex $Os_3(CO)_{11}(XPhos)$ were obtained and isolated respectively. Those crystals were characterized by X-ray diffraction (Figure 2). Additionally, it was reported that the reaction of $Os_3(CO)_{12}$ with 2-(dicyclohexylphosphino)-1-(2-methoxyphenyl)-imidazole, provides the trinuclear osmium complex, $Os_3(CO)_8L_2$.[20b] With the aspect of ruthenium carbonyl, the reaction of $Ru_3(CO)_{12}$ with dppe, *bis*-(diphenylphosphino)ethane provide $Ru(CO)_3(dppe)$,[20a] and the reaction of $Ru_3(CO)_{12}$, 1-adamantanecarboxylic acid and dppp, *bis*-(diphenylphosphino)propane, form the catalytically active mononuclear complex



Scheme 3.3. General mechanism as illustrated in the coupling of ethyl mandelate **3.1a** with 1-octene **3.2b** and stereochemical model.

$Ru(CO)(dppp)(O_2CR)_2$.[9e] Oxidative cyclometallation of the α-oxo-ester, *dehydro*-**3.1a** derived from alcohol-olefin hydrogen transfer,[17] with 1-octene **3.2b** mediated by zero-valent osmium results in the oxa-osmacycle complex **I**.[9,10] Related ruthenium(0)-mediated carbonyl-diene oxidative couplings deliver isolable metalacycles that are catalytically active and have been shown to form in a reversible manner.[9d] The next protonation process of oxa-osmacycle **I** by ethyl mandelate **3.1a** to produce the osmium alkoxide **III** will be promoted by 1-adamantanecarboxylic acid to form the osmium carboxylate **II**, which can proceed by way of a 6-centered transition structure.[13] Finally, β-Hydride elimination converts osmium alkoxide **III** to the osmium alkyl hydride complex **IV**, which upon C-H reductive elimination releases the final product **3.4a** and close the catalytic cycle. Aforementioned steric interactions as well as electronic effects[9e,12] between the *n*-hexyl side chain of 1-octene **3.2b** and the crowded osmium center contribute to branched regioselectivity.

To challenge the validity of the proposed mechanism, the following isotopic labelling experiment was conducted (Scheme 3.4). The deuterated acenaphthylene ketol *deuterio*-**3.1k** was reacted to ethylene under standard conditions. The pattern and ratio of deuterium incorporation in the adduct *deuterio*-**3.3k** was checked by ^{1}H and ^{2}H NMR. Deuterium incorporation occurs exclusively at the methyl group (22% ^{2}H), which is consistent with the proposed mechanism(Scheme 3.3). The relatively low levels of deuterium incorporation may be due to the exchange with adventitious water or with the hydroxylic proton *deuterio*-**3.1k**.[21]

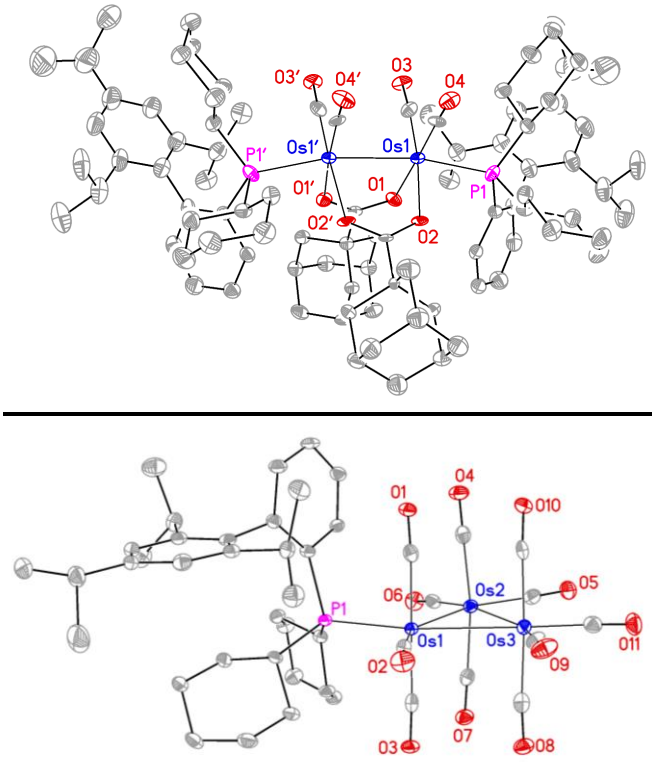
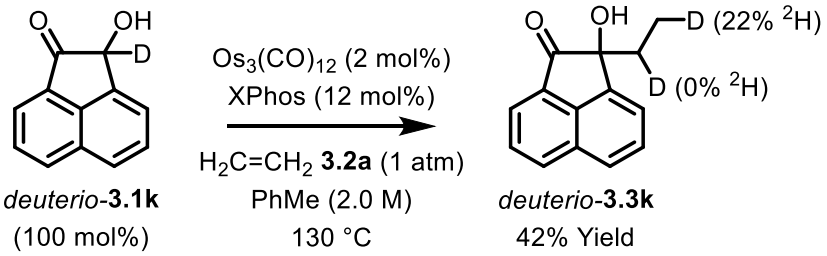


Figure 3.2. Structures of $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ (top) and $Os_3(CO)_{11}(XPhos)$ (bottom) determined by single crystal X-ray diffraction showing the atom labeling system.[a]

[a]Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity.



deuterio-**3.1k** (100 mol%)

deuterio-**3.3k** 42% Yield

Scheme 3.4. Deuterium labelling study with deuterio-**3.1k** and ethylene **3.2a**.

3.5 Summary

In summary, we found that osmium catalyst derived from $Os_3(CO)_{12}$ and XPhos enabled C-C coupling of ethylene and higher α-olefins with diverse vicinally dioxygenated hydrocarbons. Coupling may be conducted in a redox-neutral mode using α-ketols or α-hydroxy esters as reactants, or in oxidative or reductive modes using 1,2-diols or 1,2-diones as reactants, respectively. The developed catalytic reaction, which transforms abundant hydrocarbon feedstocks to value-added products in the absence of stoichiometric byproducts, represents an important objective.

3.6 Experimental Section

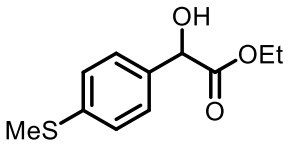
General Information: All reactions were run under an atmosphere of argon. $Os_3(CO)_{12}$, XPhos, 1-adamantanecarboxylic acid, alkenes **3.2a-3.2f**, α-hydroxy ester **3.1a**, α-ketol **3.1o**, diol *dihydro*-**3.1o**, and dione *dehydro*-**3.1k** were purchased from commercial suppliers and used as received. α-Hydroxy esters **3.1b-3.1i**[23a] were prepared in accordance with the literature procedure. α-Ketols **3.1j**,[23b] **3.1k**[23c] **3.1l**,[23b] **3.1m**,[23b] **3.1n**[23d] and diols *dihydro*-**3.1j**,[23e] *dihydro*- **3.1k**,[23f] *dihydro*-**3.1l**,[23b] **3.1m**[23g] and *dihydro*-**3.1n**[23g] were prepared using the cited literature procedures. Pressure tubes were flame dried followed by cooling in a desiccator. Toluene was dried over sodium metal-benzophenone and was distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) are reported as m/z (relative intensity) using time-of-flight (TOF) analyzers. Accurate masses are reported for the molecular ion (M+H, M+Na) or a suitable fragment ion. ^{1}H Nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in Hertz (Hz) for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.16 ppm). General Procedure A: A resealable pressure tube (15 x 100 mm, 13 mL or 15 x 125 mm, 16 mL) was charged with $Os_3(CO)_{12}$ (5.5 mg, 0.006 mmol, 2 mol%), XPhos (17.1 mg, 0.036 mmol, 12 mol%) and the reactant alcohol (0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with ethylene. Toluene (0.15 mL, 2.0 M) was added and the rubber septum was quickly replaced with a screw cap. The reaction was allowed to stir at the indicated

temperature for the stated period of time. After cooling to room temperature, the mixture was evaporated under reduced pressure and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the indicated product.

General Procedure A: A resealable pressure tube (15 x 100 mm, 13 mL or 15 x 125 mm, 16 mL) was charged with $Os_3(CO)_{12}$ (5.5 mg, 0.006 mmol, 2 mol%), XPhos (17.1 mg, 0.036 mmol, 12 mol%) and the reactant alcohol (0.30 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with ethylene. Toluene (0.15 mL, 2.0 M) was added and the rubber septum was quickly replaced with a screw cap. The reaction was allowed to stir at the indicated temperature for the stated period of time. After cooling to room temperature, the mixture was evaporated under reduced pressure and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the indicated product.

General Procedure B: A resealable pressure tube (13 x 100 mm, 9 mL) was charged with $Os_3(CO)_{12}$ (3.7 mg, 0.004 mmol, 2 mol%), XPhos (11.4 mg, 0.024 mmol, 12 mol%), $AdCO_2H$ (3.6 mg, 0.02 mmol, 10 mol%) and the reactant alcohol (0.20 mmol, 100 mol%). The tube was sealed with a rubber septum and purged with argon. 1-Octene (112.2 mg, 1.0 mmol, 500 mol%) was added *via* syringe and the rubber septum was quickly replaced with a screw cap. The reaction was allowed to stir at the indicated temperature for the stated period of time. After cooling to room temperature, the mixture was evaporated under reduced pressure and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the indicated product.

Ethyl 2-hydroxy-2-(4-(methylthio)phenyl)acetate (3.1g).



To a flame-dried 50 mL round-bottom flask charged with ethyl 2-hydroxy-2-(4-(methylthio)phenyl)acetate (1.1 g, 4.9 mmol), was added ethanol (25 mL, 0.2 M). $NaBH_4$ (200 mg, 5.3 mmol) was added portionwise. The reaction mixture was allowed to stir at ambient temperature until the suspension became colorless. Distilled water was added and the reaction mixture was allowed to stir until bubbling stopped. The mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine (1 x 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2: 20% ethyl acetate in hexanes) to give the title compound (0.93g, 4.1 mmol) in 84% yield as a white solid.

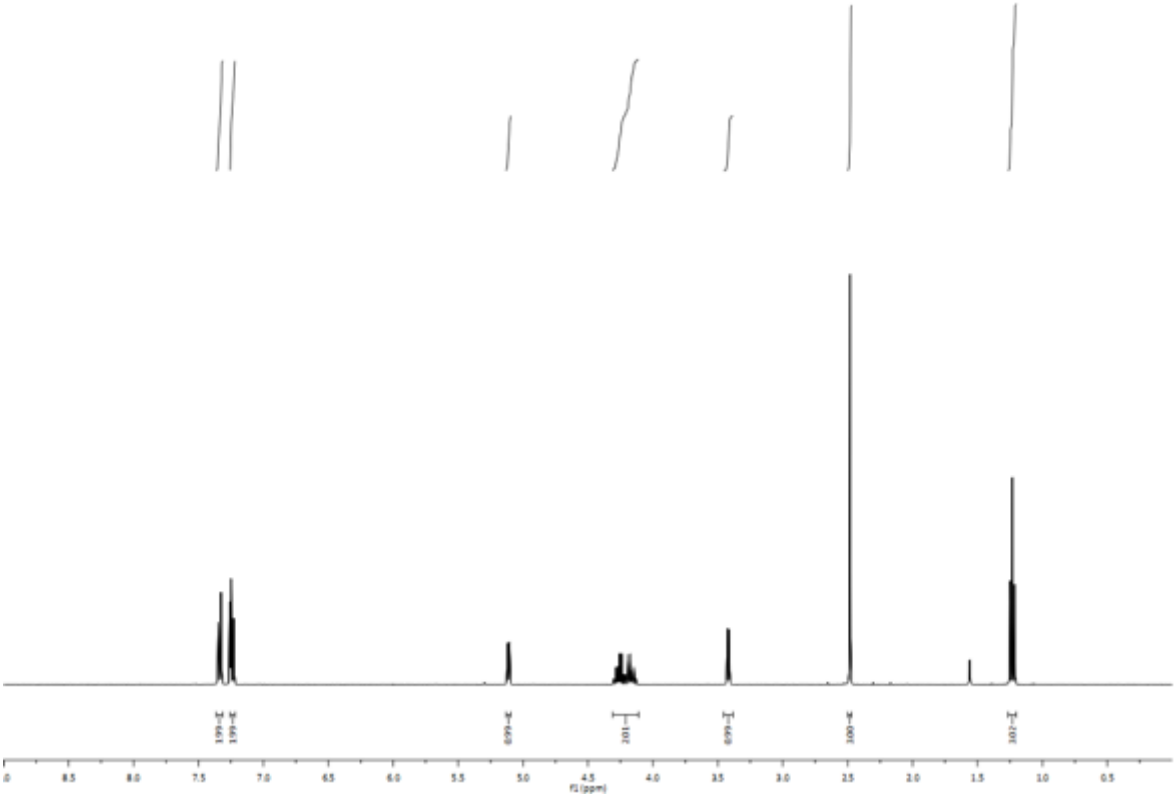
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.11 (d, *J* = 8.0 Hz 1H), 4.22 (m, 2H), 3.42 (d, *J* = 8.0 Hz, 1H), 2.48 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm.

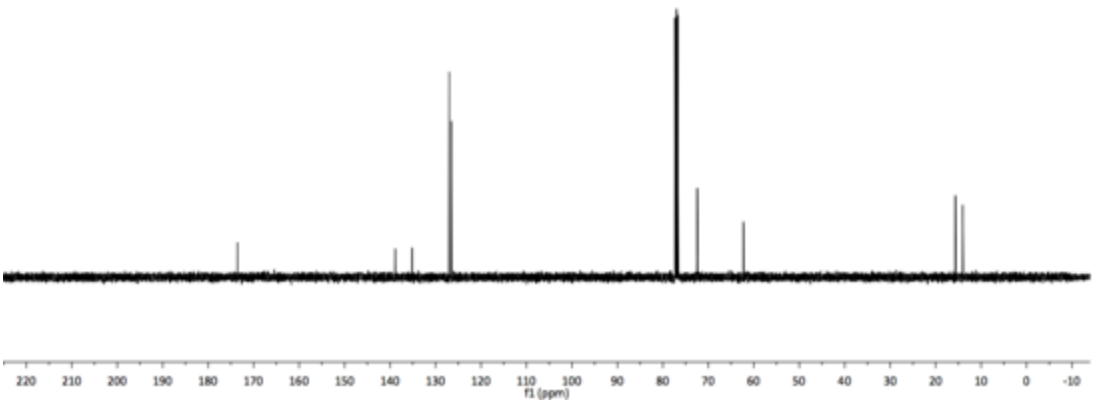
^{13}C NMR: ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 138.9, 135.2, 127.0, 126.5, 72.5, 62.3, 15.7, 14.0 ppm.

MP: 91 ^{o}C.

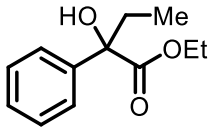
HRMS: (ESI-MS) Calcd. for $C_{11}H_{14}O_3S$ $[M+Na]^+$: 249.0556, Found: 249.0557

FTIR: (neat): 3438, 2979, 1726 cm^{-1}.


1.61
1.61
0.69
1.01
0.69
3.00
1.01
f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-2-phenylbutanoate (3.3a).



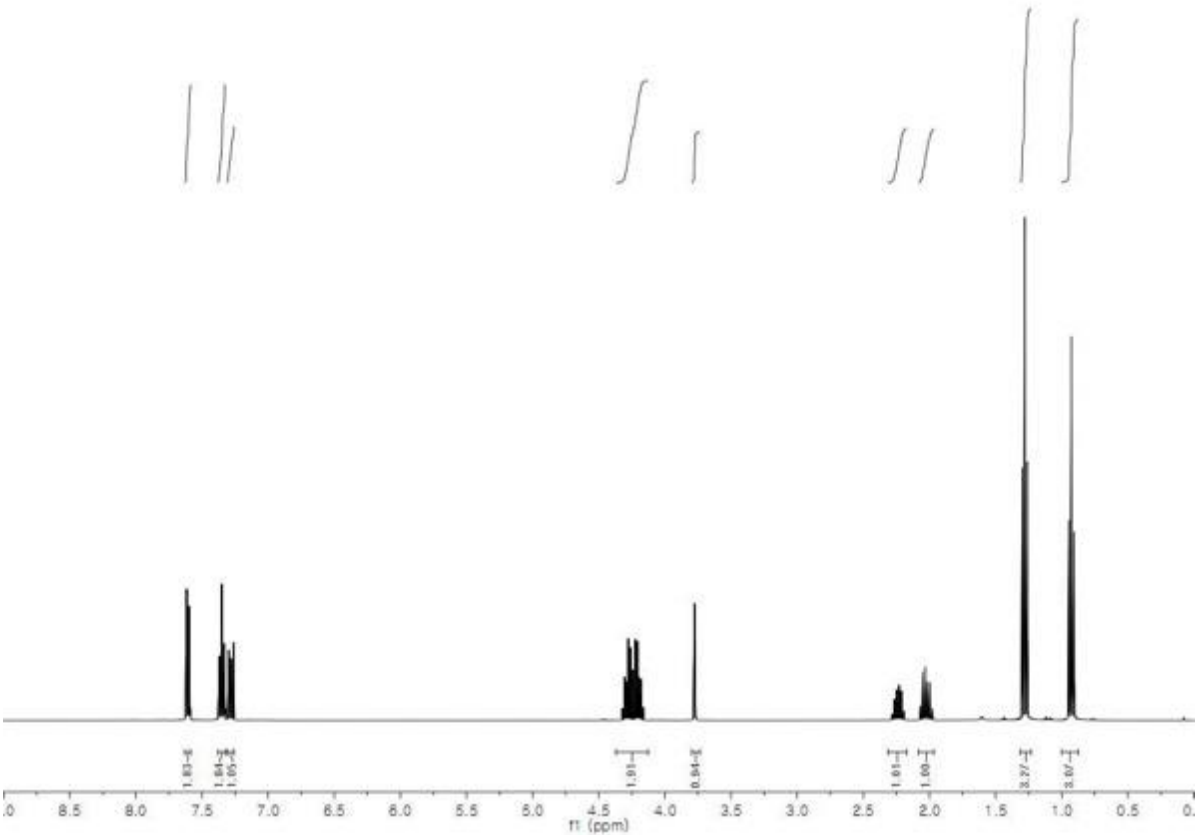
In accordance with general procedure A, **3.1a** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2-5% ether/hexanes) provided the title compound (48.7 mg, 0.23 mmol) as a yellow oil in 78% yield.

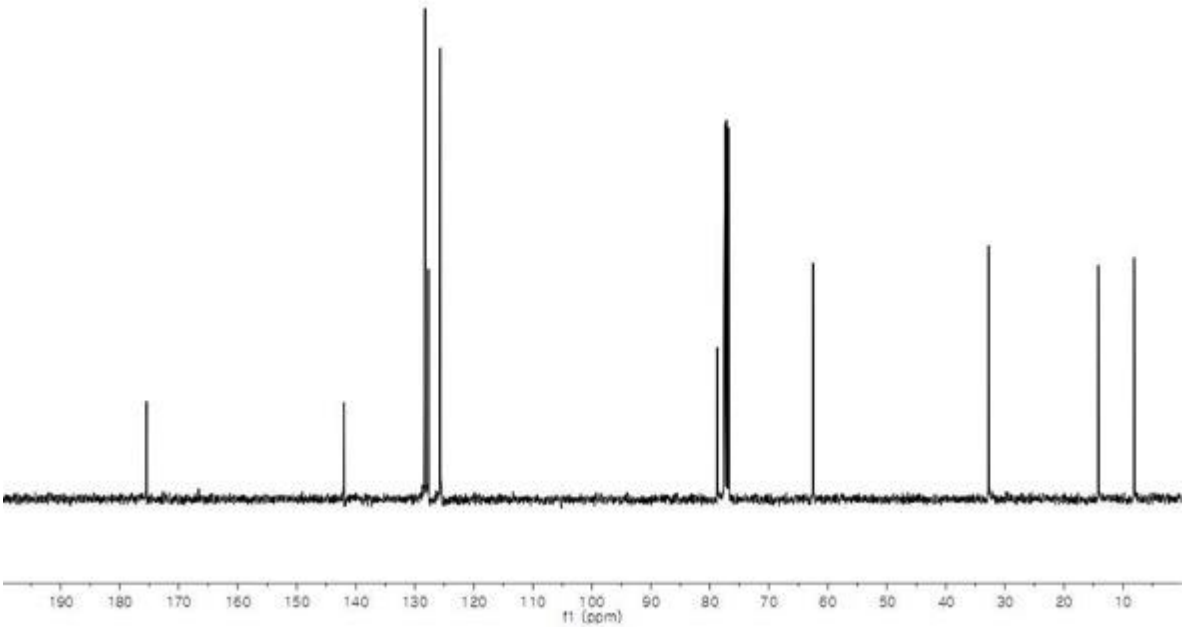
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.59 (m, 2H), 7.37–7.32 (m, 2H), 7.30–7.26 (m, 1H), 4.32–4.16 (m, 2H), 3.78 (d, *J* = 0.4 Hz, 1H), 2.24 (dqd, *J* = 14.4, 7.2, 0.8 Hz, 1H), 2.07–1.98 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 142.0, 128.3, 127.7, 125.7, 78.7, 62.5, 32.8, 14.2, 8.2 ppm.

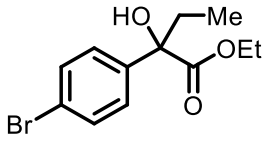
LRMS (ESI) Calcd. for $C_{12}H_{16}O_3$, [M+Na]+: 231, Found: 231

FTIR (neat): 3504, 2980, 1721.


1.83
1.84
1.95
1.91
0.84
1.91
1.88
3.27
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-(4-bromophenyl)-2-hydroxybutanoate (3.3b).



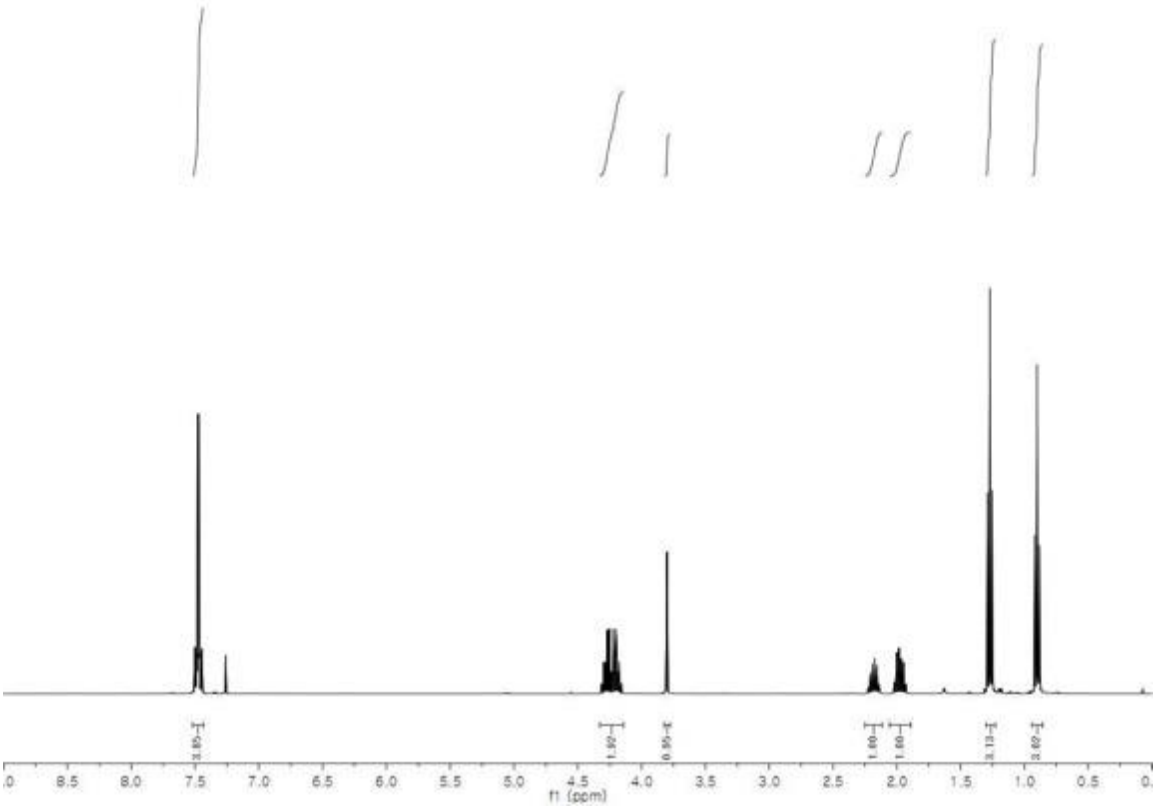
In accordance with Procedure A, **3.1b** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2-4% ether/hexanes) provided the title compound (63.7 mg, 0.22 mmol) as a yellow oil in 74% yield.

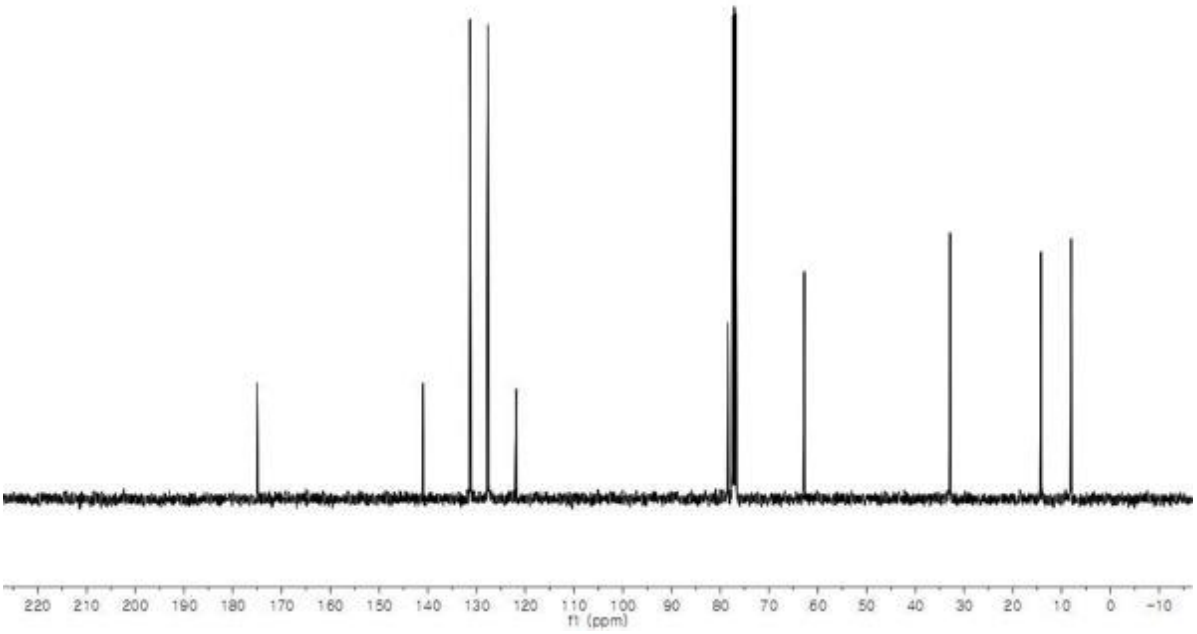
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.44 (m, 4H), 4.32–4.15 (m, 2H), 3.80 (d, *J* = 0.5 Hz, 1H), 2.24–2.12 (m, 1H), 1.97 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.99 (dd, *J* = 9.5, 5.2 Hz, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 141.0, 131.4, 127.7, 121.9, 78.4, 62.8, 32.9, 14.2, 8.1 ppm.

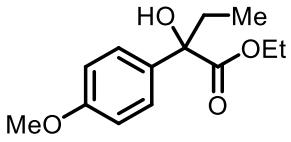
LRMS (ESI) Calcd. for $C_{12}H_{15}BrO_3$, $[M+Na]^+$: 309, 311, Found: 309, 311

FTIR (neat): 3499, 2980, 1723.


f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-2-(4-methoxyphenyl)butanoate (3.3c).



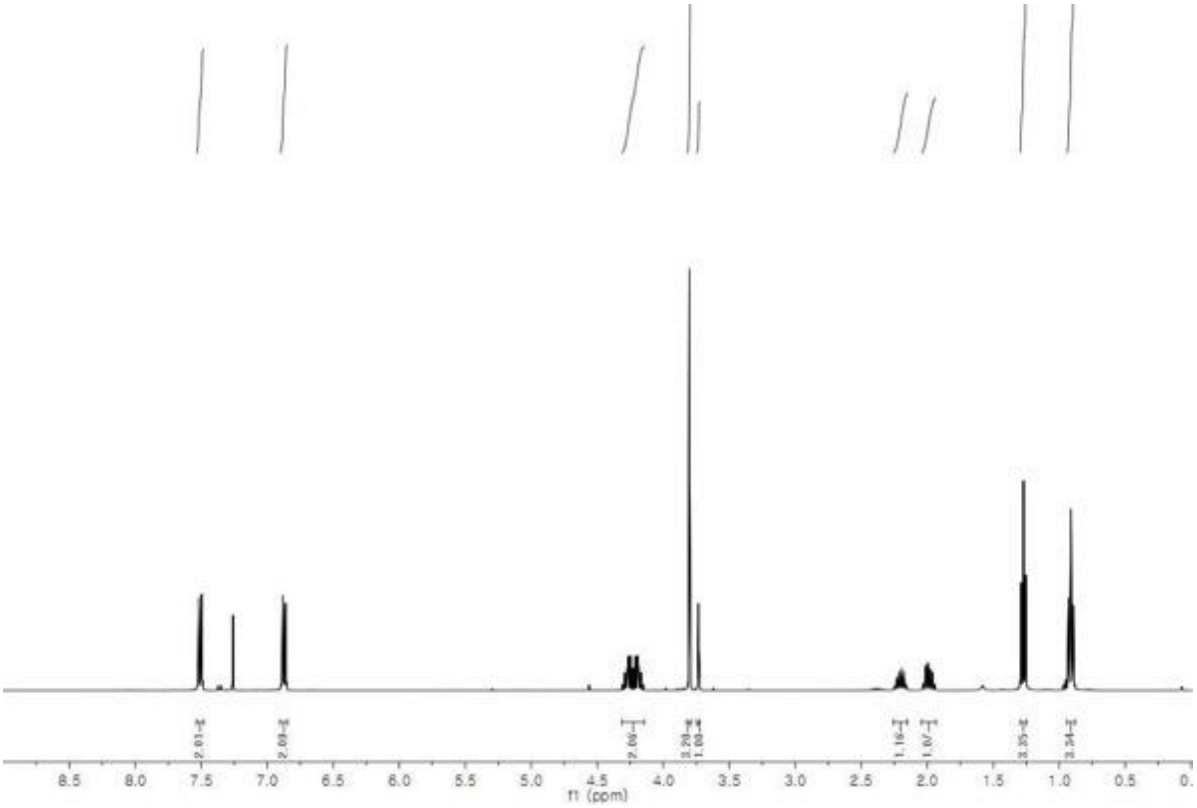
In accordance with Procedure A, **3.1c** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 ºC for a 40 hour period. Flash column chromatography (SiO_2: 50-100% dichloromethane/hexanes to 5% ethyl acetate/hexanes) provided the title compound (43.6 mg, 0.18 mmol) as a yellow oil in 61% yield.

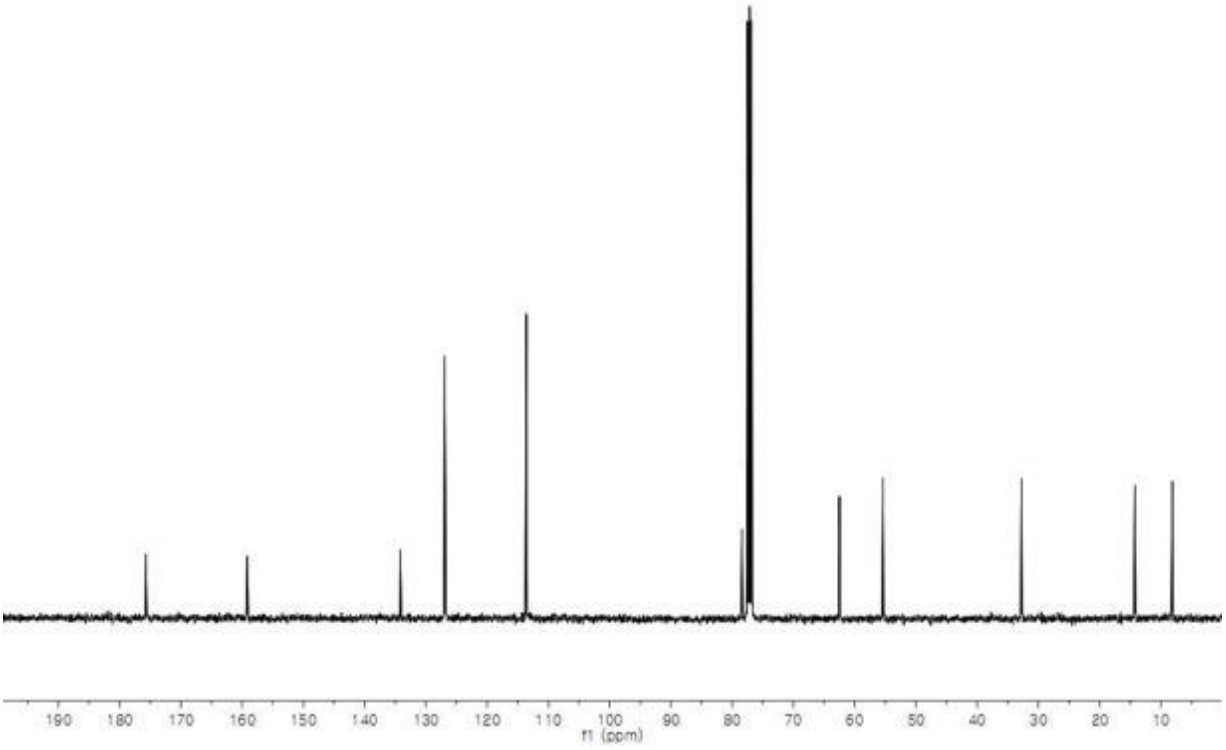
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.48 (m, 2H), 6.90–6.85 (m, 2H), 4.31–4.14 (m, 2H), 3.80 (s, 3H), 3.73 (s, 1H), 2.26–2.15 (m, 1H), 1.99 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 159.1, 134.2, 126.9, 113.6, 78.4, 62.5, 55.4, 32.8, 14.3, 8.2 ppm

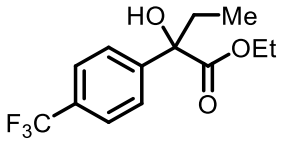
LRMS (ESI) Calcd. for $C_{13}H_{18}O_4$, $[M+Na]^+$: 261, Found: 261

FTIR (neat): 3511, 2970, 1721.


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-hydroxy-2-(4-(trifluoromethyl)phenyl)butanoate (3.3d).



In accordance with Procedure A, **3.1d** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 1-5% ether/hexanes) provided the title compound (63.8 mg, 0.23 mmol) as a yellow oil in 77% yield.

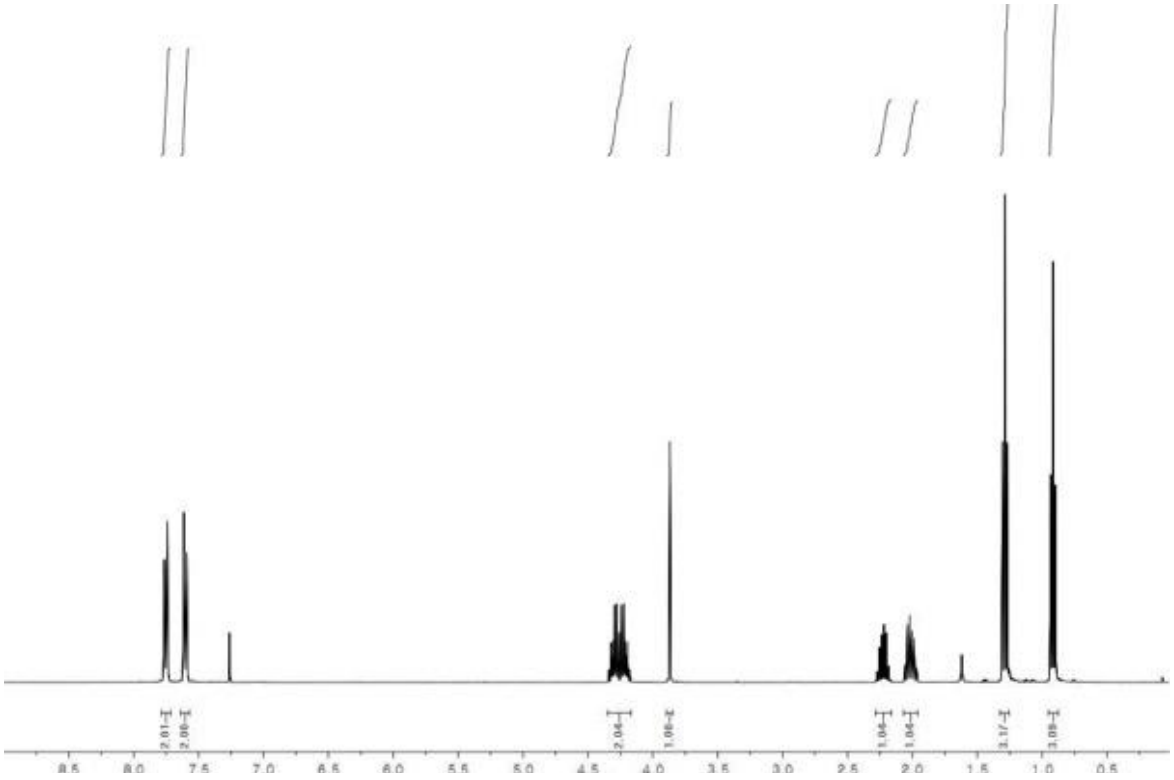
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.72 (m, 2H), 7.64–7.57 (m, 2H), 4.35–4.17 (m, 2H), 3.87 (s, 1H), 2.23 (dq, *J* = 14.5, 7.2 Hz, 1H), 2.01 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.28 (t, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm

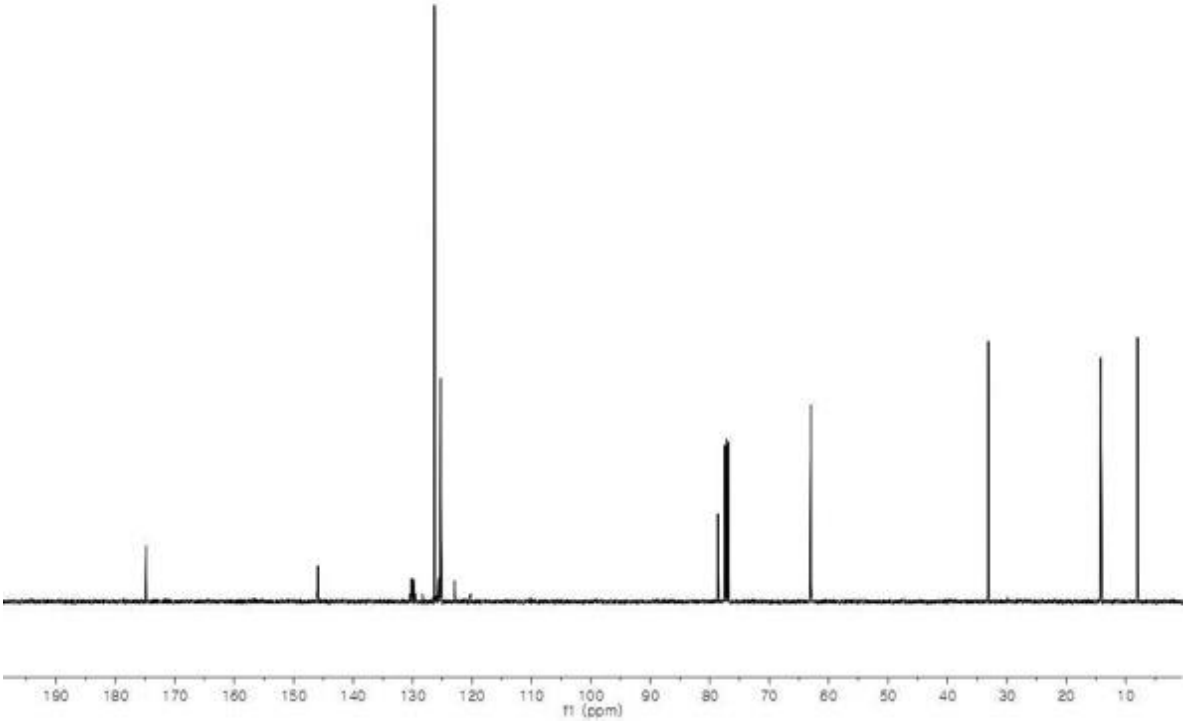
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 145.9, 130.0 (q, *J* = 32.0 Hz), 126.3, 125.2 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 271.0 Hz), 78.6, 63.0, 33.1, 14.2, 8.0 ppm.

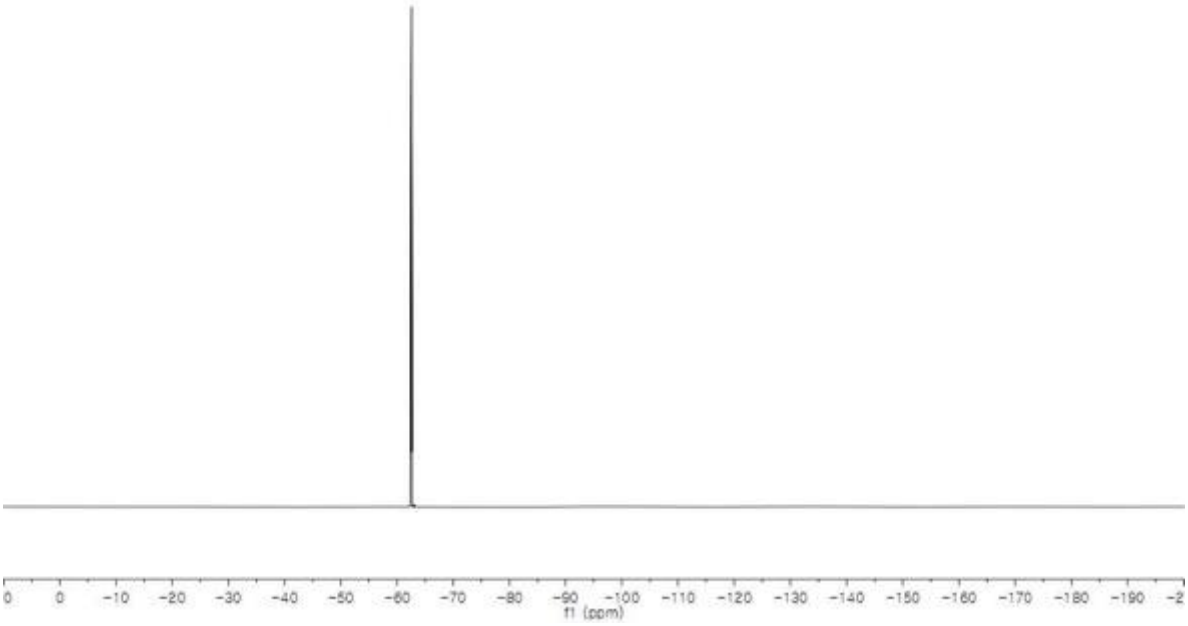
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6 ppm

LRMS (ESI) Calcd. for $C_{13}H_{15}F_3O_3$, $[M+Na]^+$: 299, Found: 299

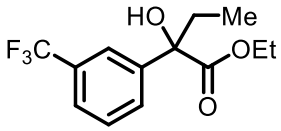
FTIR (neat): 3510, 2985, 1726.


2.01
2.00
2.04
1.00
1.04
1.04
3.17
3.09


f1 (ppm)


0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

Ethyl 2-hydroxy-2-(3-(trifluoromethyl)phenyl)butanoate (3.3e).



In accordance with Procedure A, **3.1e** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2-5% ether/hexanes) provided the title compound (63.0 mg, 0.23 mmol) as a yellow oil in 76% yield.

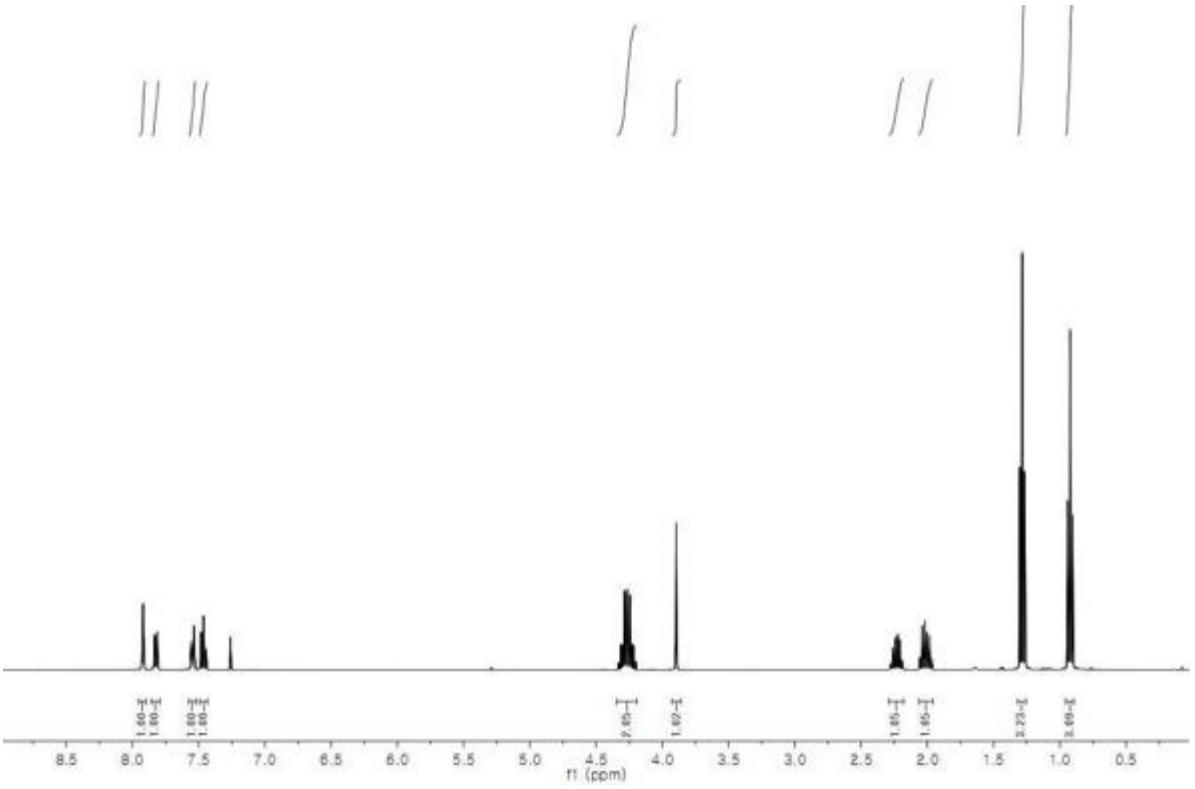
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.86–7.79 (m, 1H), 7.55 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.46 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.34–4.19 (m, 2H), 3.90 (d, *J* = 0.5 Hz, 1H), 2.29–2.18 (m, 1H), 2.01 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm

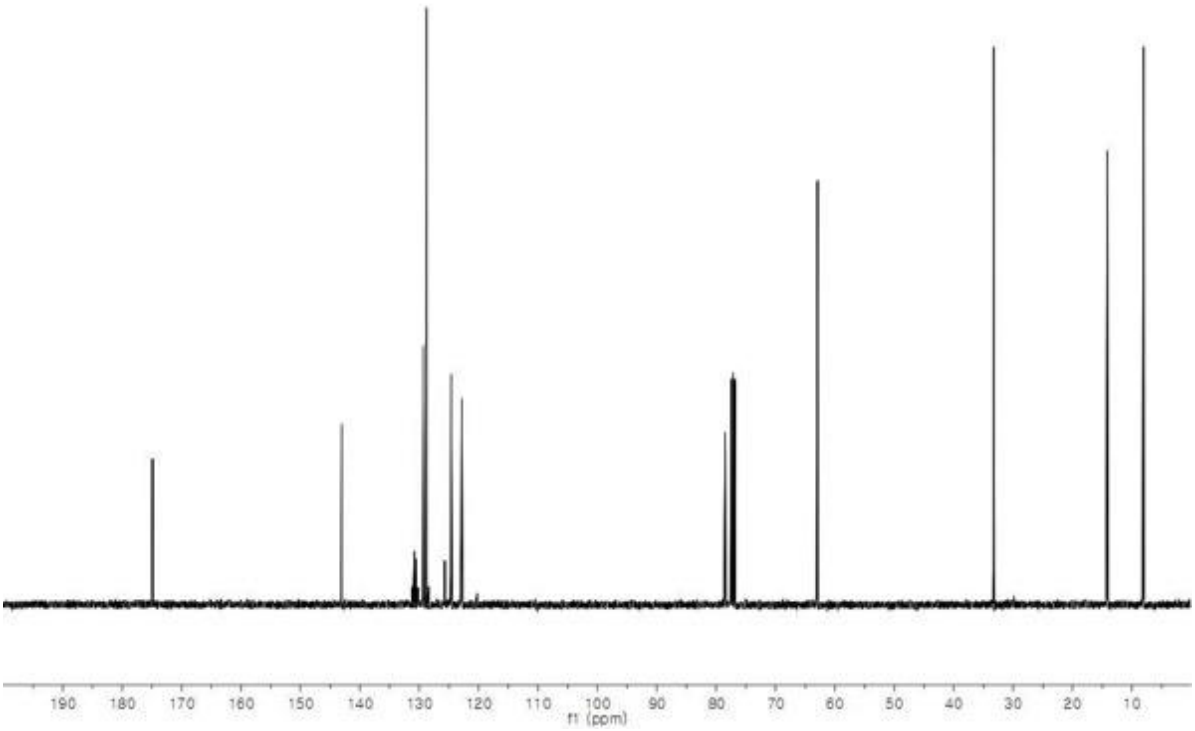
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 143.1, 130.7 (q, *J* = 32.0 Hz), 129.3, 128.8, 124.6 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.0 Hz), 122.9 (q, *J* = 4.0 Hz), 78.5, 63.0, 33.2, 14.2, 8.1 ppm.

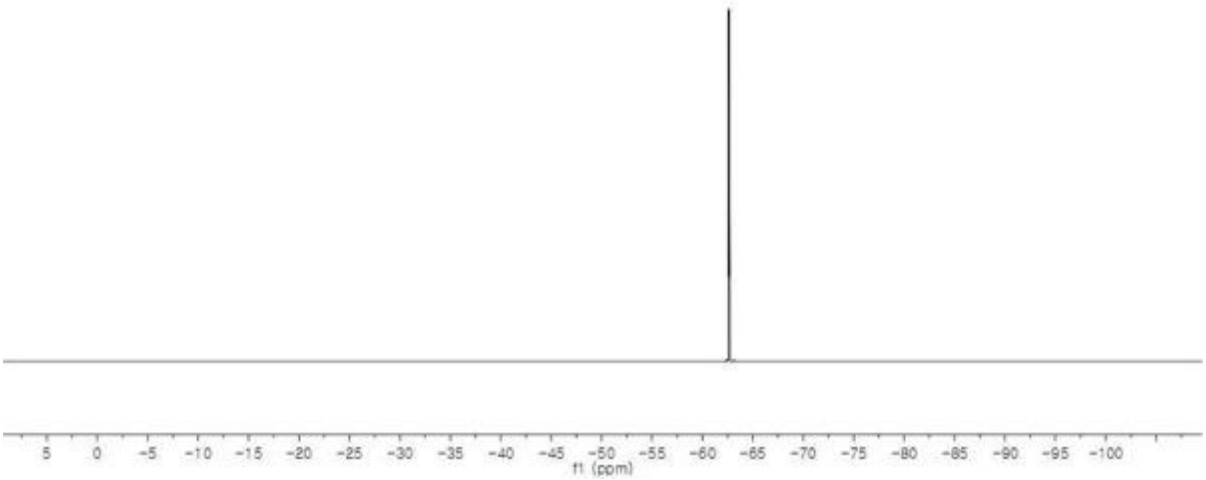
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6 ppm

LRMS (ESI) Calcd. for $C_{13}H_{15}F_3O_3$, $[M+Na]^+$: 299, Found: 299

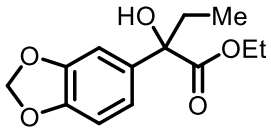
FTIR (neat): 3513, 2985, 1725.


1.00
1.00
1.00
1.00
2.65
1.67
1.65
1.65
3.73
3.69
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)

Ethyl 2-(benzo[d][1,3]dioxol-5-yl)-2-hydroxybutanoate (3.3f).



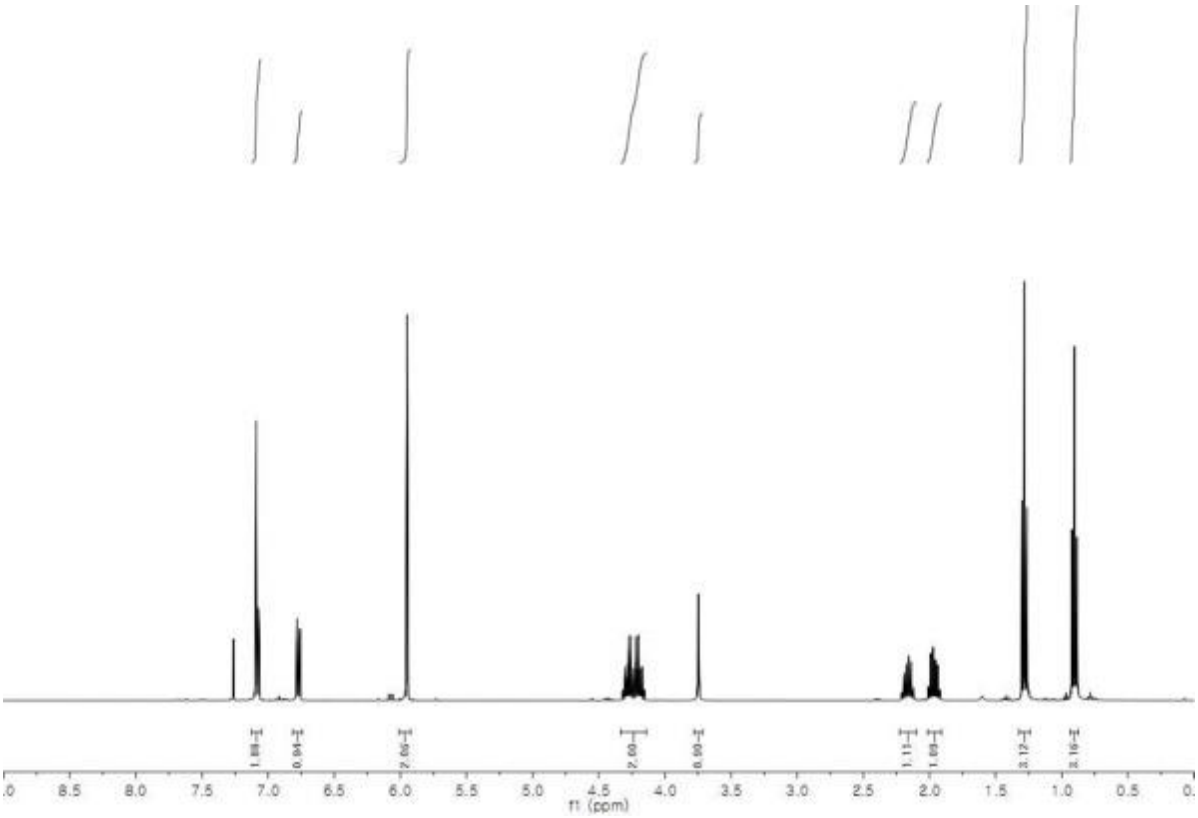
In accordance with Procedure A, **3.1f** (0.2 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 290 mol%) in toluene (2.0 M) at 140 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 3-5% ether/hexanes) provided the title compound (30.8 mg, 0.12 mmol) as a colorless oil in 61% yield. NOTE: $Os_3(CO)_{12}$ (3.6 mg, 0.004 mmol, 2 mol%) and XPhos (11.4 mg, 0.024 mmol, 12 mol%).

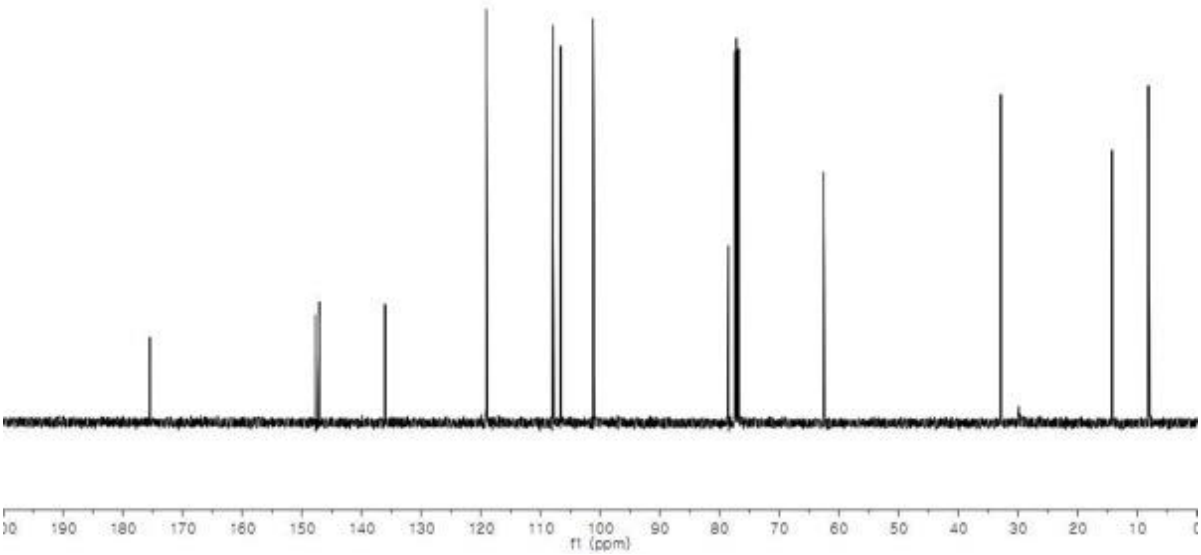
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.05 (m, 2H), 6.77 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.01–5.92 (m, 2H), 4.33–4.14 (m, 2H), 3.75 (s, 1H), 2.16 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.96 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 147.7, 147.1, 136.1, 119.1, 107.9, 106.7, 101.2, 78.5, 62.6, 32.9, 14.3, 8.1 ppm.

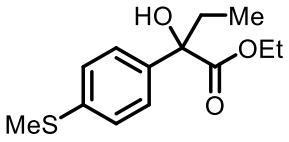
LRMS (ESI) Calcd. for $C_{13}H_{16}O_5$, $[M+Na]^+$: 275, Found: 275.

FTIR (neat): 3507, 2971, 1722.


1.81
4.00
2.00
0.99
1.11
1.01
3.12
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-hydroxy-2-(4-(methylthio)phenyl)butanoate (3.3g).



In accordance with Procedure A, **3.1g** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2-5% ether/hexanes) provided the title compound (30.8 mg, 0.18 mmol) as a yellow oil in 61% yield.

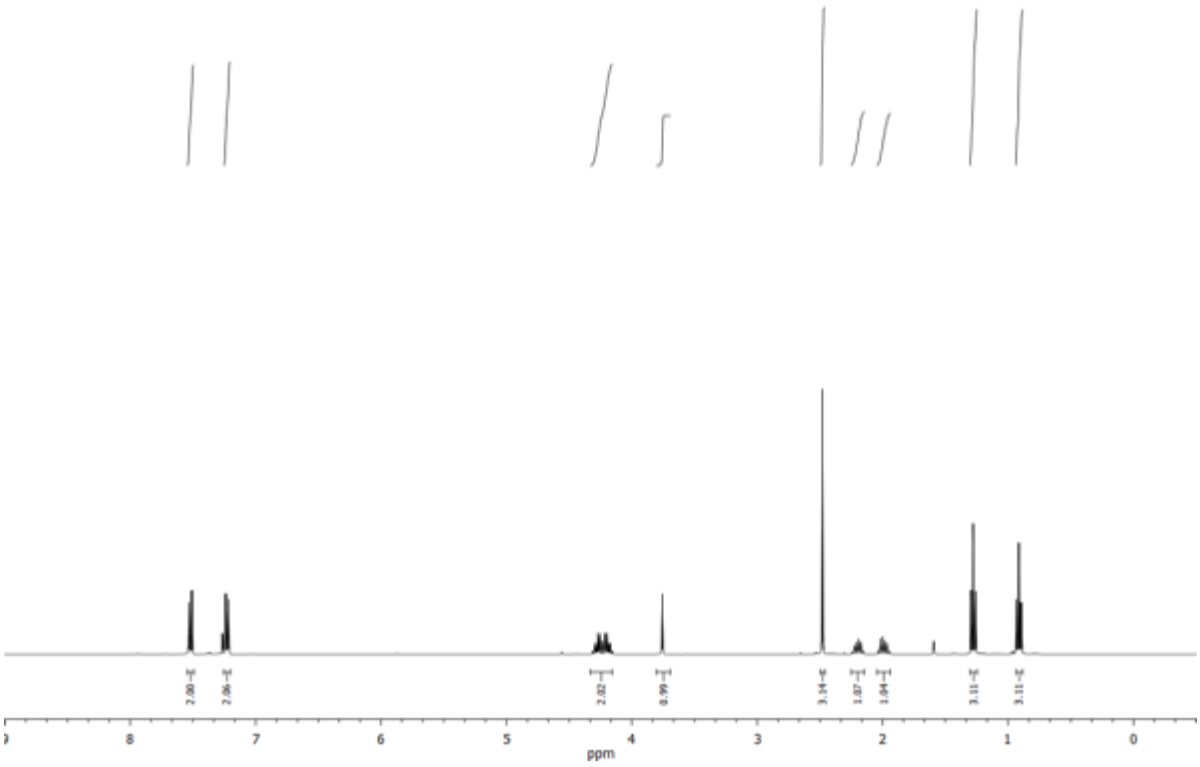
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.48 (m, 2H), 7.26–7.20 (m, 2H), 4.37–4.10 (m, 2H), 3.76 (s, 1H), 2.48 (s, 3H), 2.25–2.15 (m, 1H), 2.04-1.95 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

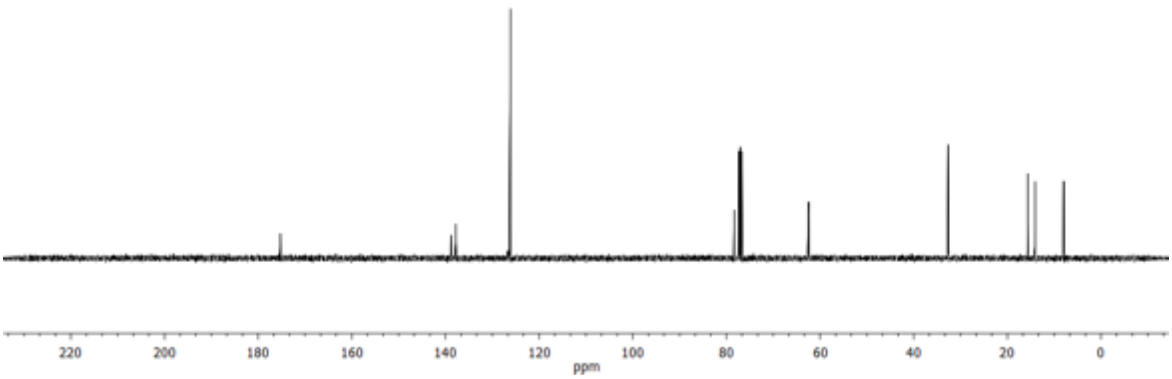
^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 138.7, 137.8, 126.2, 126.1 78.3, 62.4, 32.6, 15.7, 14.1, 7.9 ppm.

LRMS (ESI) Calcd. for $C_{13}H_{18}O_3S$, $[M+Na]^+$: 277, Found: 277

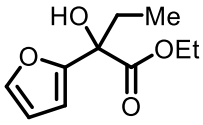
FTIR (neat): 3507, 2979, 1721.

.


2.00
2.06
2.02
0.99
3.14
1.07
1.04
3.11
3.11
8
7
6
5
4
3
2
1
0
ppm


220
200
180
160
140
120
100
80
60
40
20
0
ppm

Ethyl 2-(furan-2-yl)-2-hydroxybutanoate (3.3h).



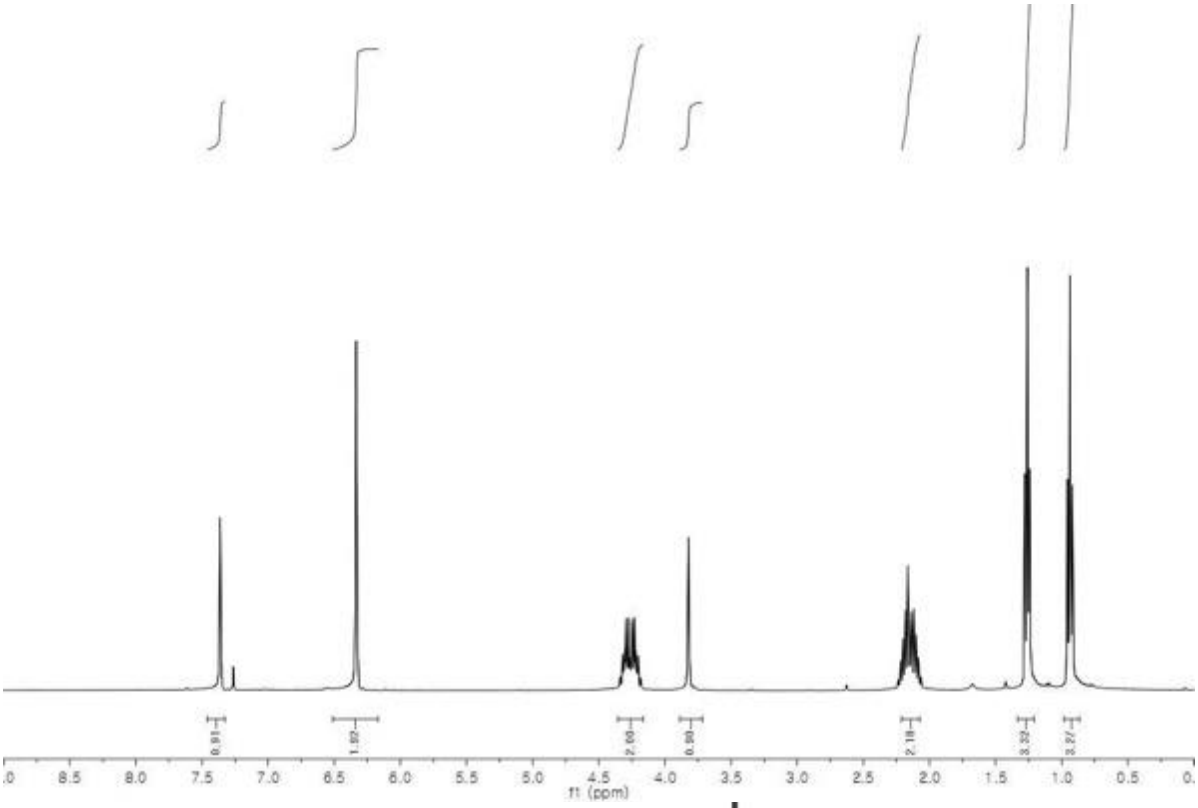
In accordance with Procedure A, **3.1h** (0.2 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 290 mol%) in toluene (2.0 M) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 3-5% ether/hexanes) provided the title compound (25.0 mg, 0.13 mmol) as a yellow oil in 64% yield.

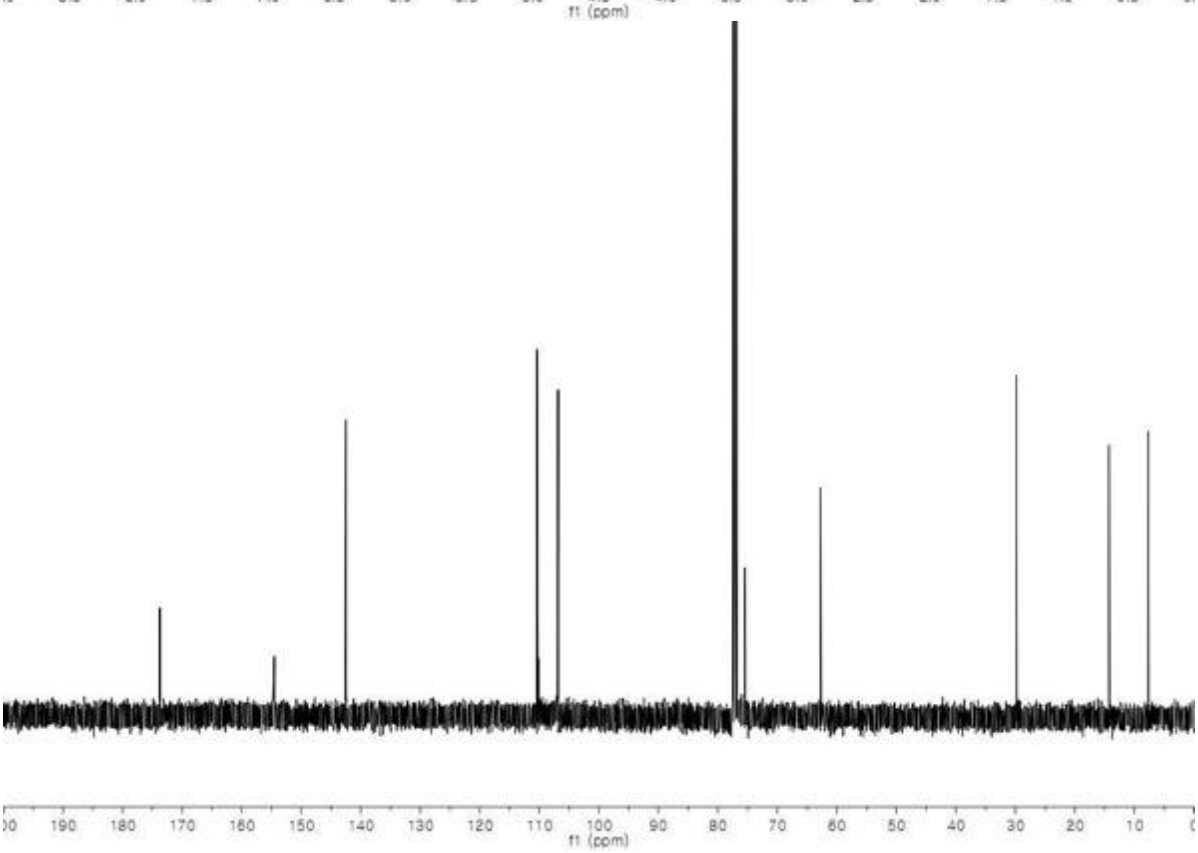
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 1.1 Hz, 1H), 6.33 (s, 2H), 4.36–4.14 (m, 2H), 3.82 (s, 1H), 2.21–2.07 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 154.5, 142.5, 110.4, 106.8, 75.5, 62.8, 29.8, 14.3, 7.7 ppm

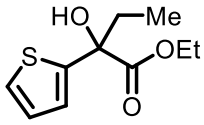
LRMS (ESI) Calcd. for $C_{10}H_{14}O_4$, $[M+Na]^+$: 221, Found: 221.

FTIR (neat): 3511, 2970, 1728.


0.91
1.02
2.00
0.90
2.18
3.22
3.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-hydroxy-2-(thiophen-2-yl)butanoate (3.3i).



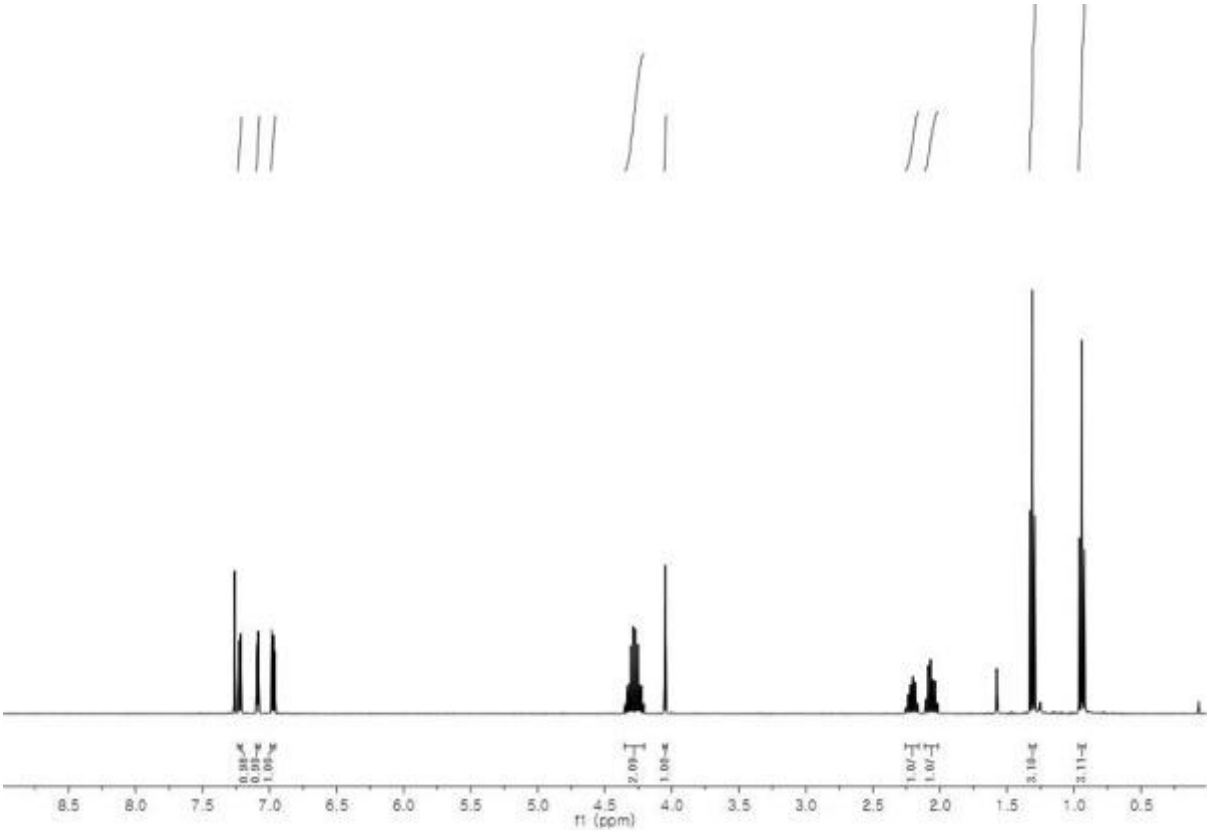
In accordance with Procedure A, **3.1i** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 30-50% dichloromethane/hexanes) provided the title compound (45.0 mg, 0.22 mmol) as a colorless oil in 70% yield.

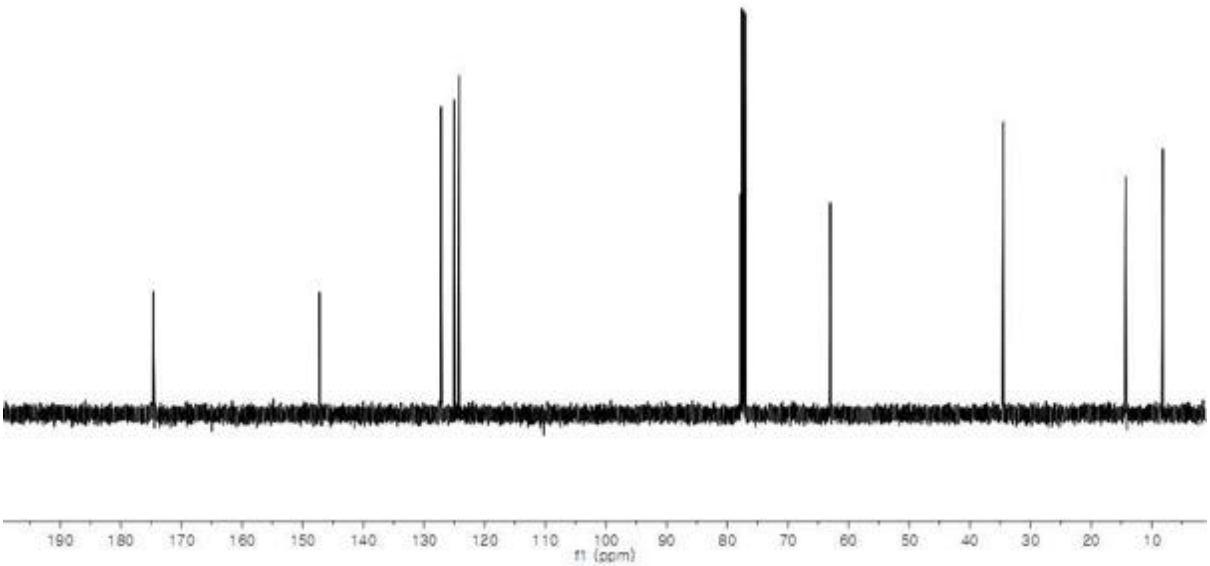
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.35–4.21 (m, 2H), 4.05 (d, *J* = 0.8 Hz, 1H), 2.26–2.16 (m, 1H), 2.06 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 147.1, 127.1, 124.9, 124.1, 77.7, 62.9, 34.4, 14.2, 8.1 ppm.

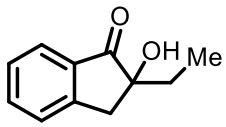
LRMS (ESI) Calcd. for $C_{10}H_{14}O_3S$, $[M+Na]^+$: 237, Found: 237

FTIR (neat): 3499, 2979, 1724.


0.98
0.95
1.00
2.69
1.00
1.07
1.07
3.18
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2-Ethyl-2-hydroxy-2,3-dihydro-1H-inden-1-one (3.3j).



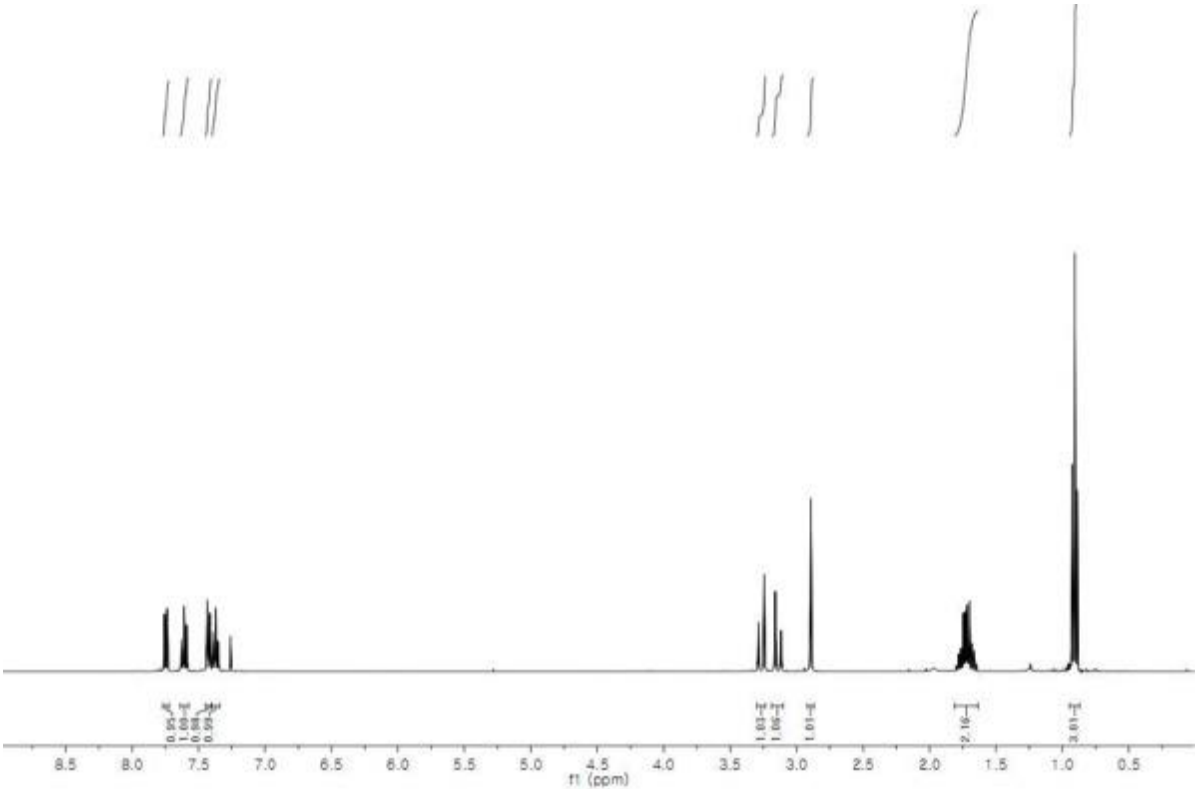
(Using ketol) In accordance with Procedure A, **3.1j** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 140 °C for a 40 hour period. Flash column chromatography (SiO_2: 5-15% ethyl acetate/hexanes) provided the title compound (44.4 mg, 0.25 mmol) as a yellow oil in 84% yield. (**Using diol)** In accordance with Procedure A, H_2-**3.1j** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 390 mol%) in toluene (1.5 M) at 140 °C for a 48 hour period. Flash column chromatography (SiO_2: 5-15% ethyl acetate/hexanes) provided the title compound (18.8 mg, 0.11 mmol) as a yellow oil in 71% yield. NOTE: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol%), XPhos (8.5 mg, 0.018 mmol, 12 mol%).

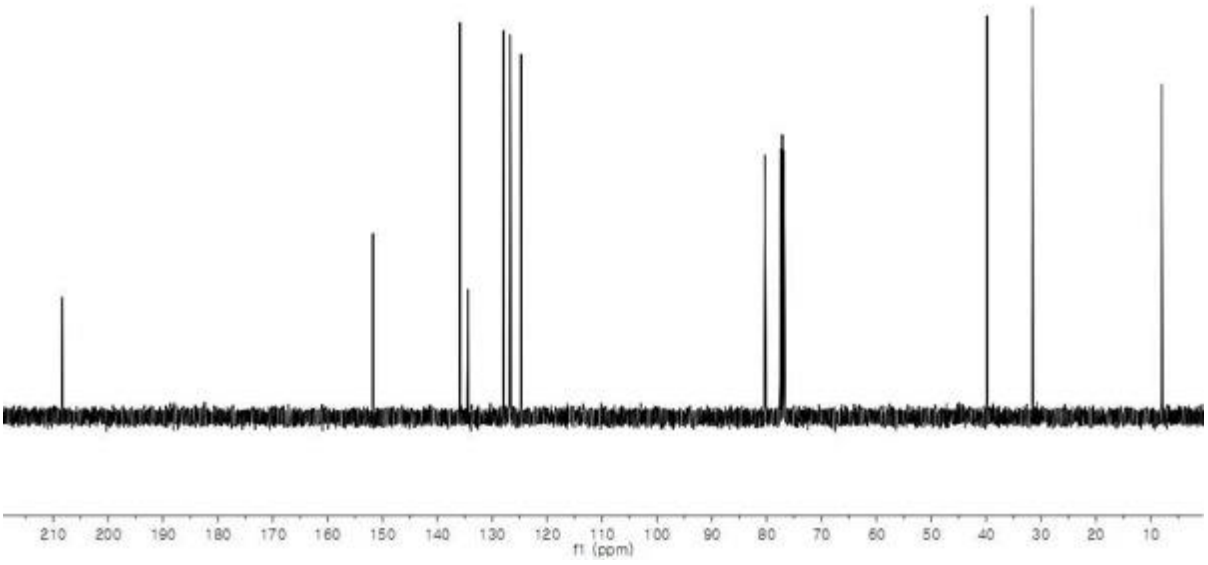
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.72 (m, 1H), 7.61 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.45–7.41 (m, 1H), 7.40–7.34 (m, 1H), 3.27 (d, *J* = 17.0 Hz, 1H), 3.14 (d, *J* = 17.0 Hz, 1H), 2.89 (s, 1H), 1.81–1.64 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 151.7, 135.9, 134.4, 127.9, 126.7, 124.7, 80.3, 39.8, 31.6, 8.0 ppm.

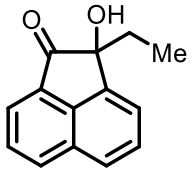
LRMS (ESI) Calcd. for $C_{11}H_{12}O_2$, $[M+Na]^+$: 199, Found: 199

FTIR (neat): 3413, 2967, 1709.


0.95
1.00
0.84
0.99
1.03
1.00
1.01
2.16
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-Ethyl-2-hydroxyacenaphthylen-1(2H)-one (3.3k).



(Using ketol) In accordance with Procedure A, **3.1k** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 ^{o}C for a 48 hour period. Flash column chromatography (SiO_2: 5-15% ethyl acetate/hexanes) provided the title compound (40.1 mg, 0.18 mmol) as a yellow solid in 63% yield. **(Using diol)** In accordance with Procedure A, H_2-**3.1k** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 125 mm pressure tube, 0.71 mmol, 480 mol%) in toluene (1.5 M) at 140 ^{o}C for a 48 hour period. Flash column chromatography (SiO_2: 5-15% ethyl acetate/hexanes) provided the title compound (21.3 mg, 0.11 mmol) as a yellow solid in 70% yield. NOTE: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol%), XPhos (8.5 mg, 0.018 mmol, 12 mol%) and $AdCO_2H$ (2.7 mg, 0.015mmol, 10 mol%).

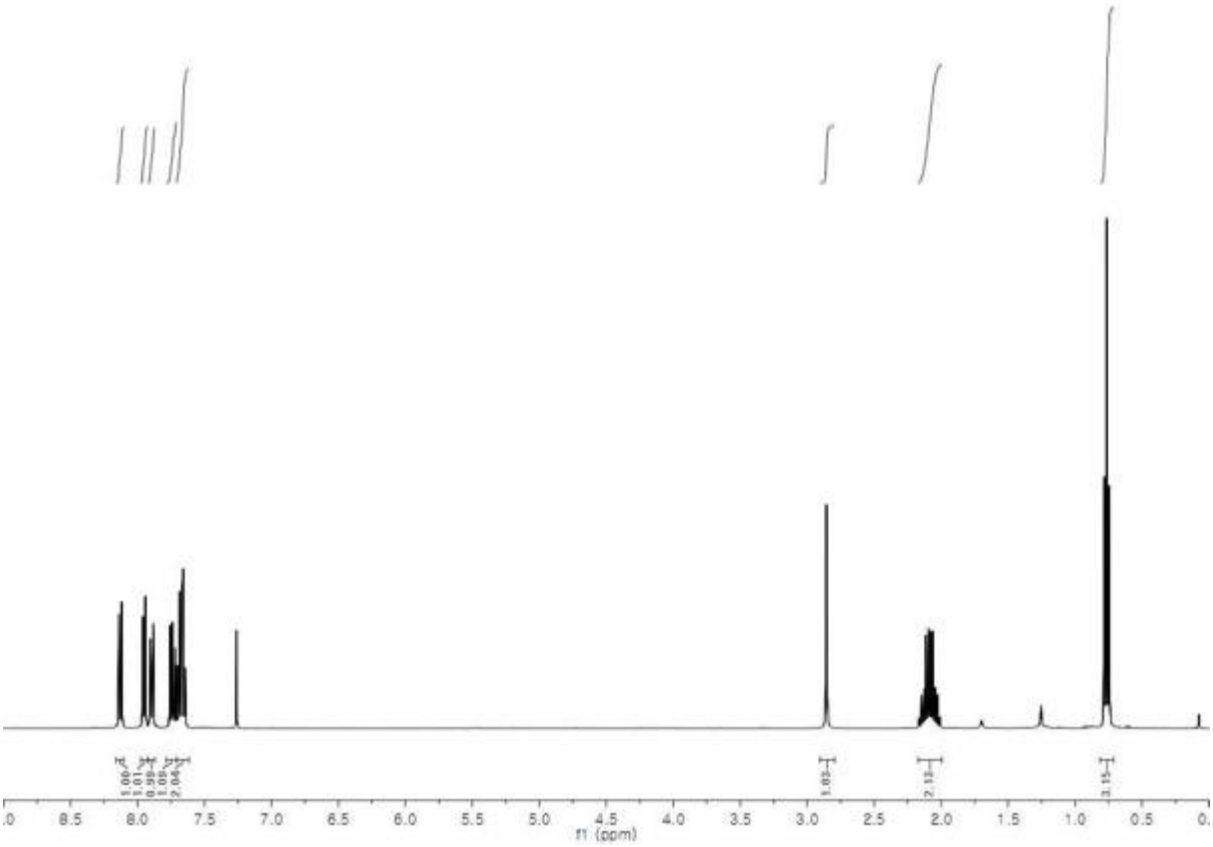
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.74 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.71–7.62 (m, 2H), 2.86 (s, 1H), 2.17–1.99 (m, 2H), 0.76 (t, *J* = 7.5 Hz, 3H) ppm.

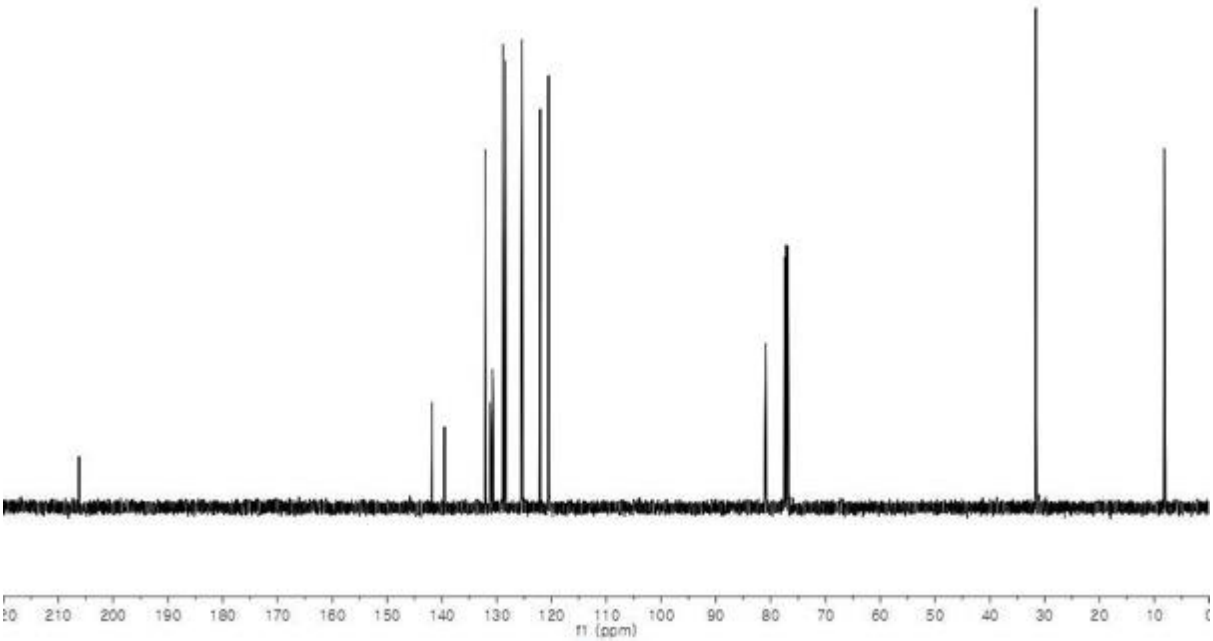
^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 141.8, 139.5, 132.1, 131.2, 130.8, 128.9, 128.4, 125.4, 122.0, 120.5, 80.9, 31.6, 8.2 ppm.

LRMS (ESI) Calcd. for $C_{14}H_{12}O_2$, $[M+Na]^+$: 235, Found: 235

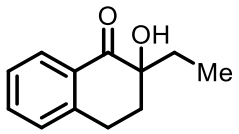
FTIR (neat): 3369, 2970, 2931, 1716.

MP: 92.7–93.1 ^{o}C


f1 (ppm)


f1 (ppm)

2-Ethyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (3.3l).



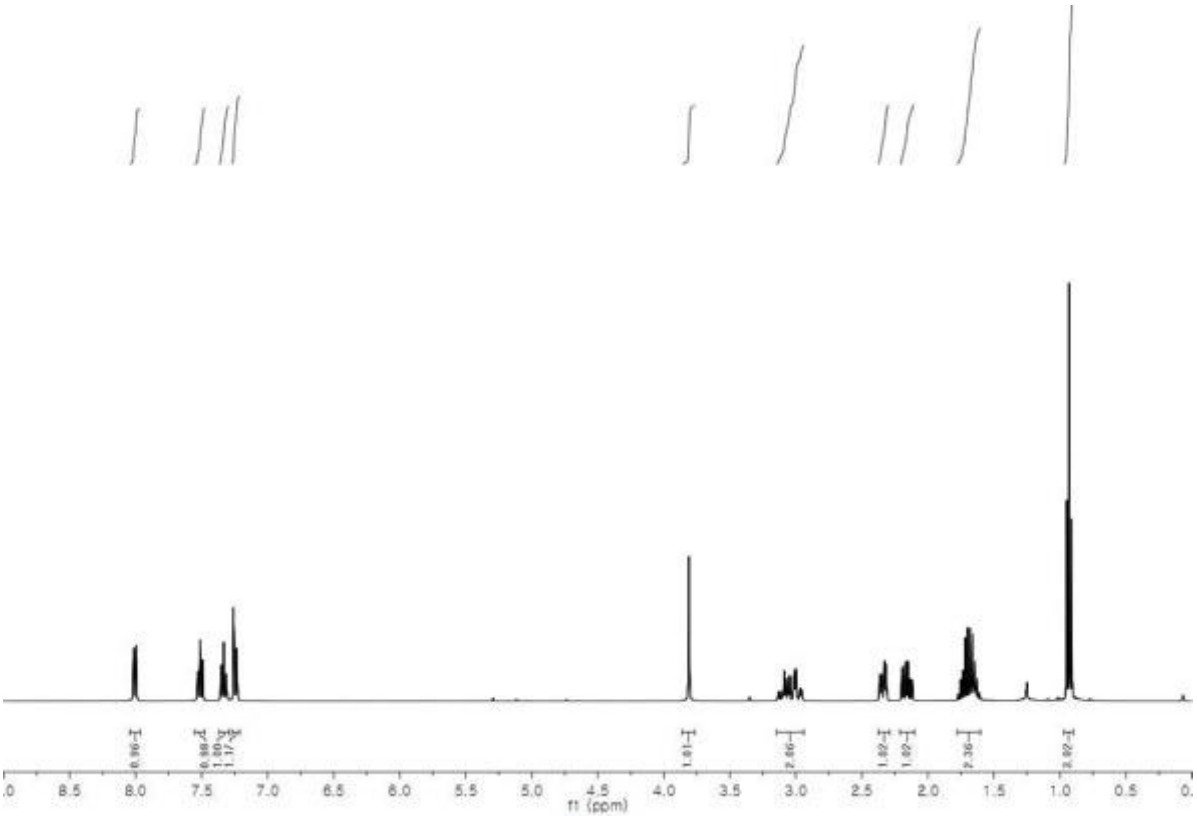
(Using ketol) In accordance with Procedure A, **3.1l** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 140 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (47.4 mg, 0.25 mmol) as a brown oil in 83% yield. NOTE: $AdCO_2H$ (5.4 mg, 0.03mmol, 10 mol%). **(Using diol)** In accordance with Procedure A, H_2-**3.1l** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 125 mm pressure tube, 0.71 mmol, 480 mol%) in toluene (1.5 M) at 140 ^{o}C for a 48 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (20.3 mg, 0.11 mmol) as a brown oil in 71% yield. NOTE: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol%), XPhos (8.5 mg, 0.018 mmol, 12 mol%) and $AdCO_2H$ (2.7 mg, 0.015mmol, 10 mol%).

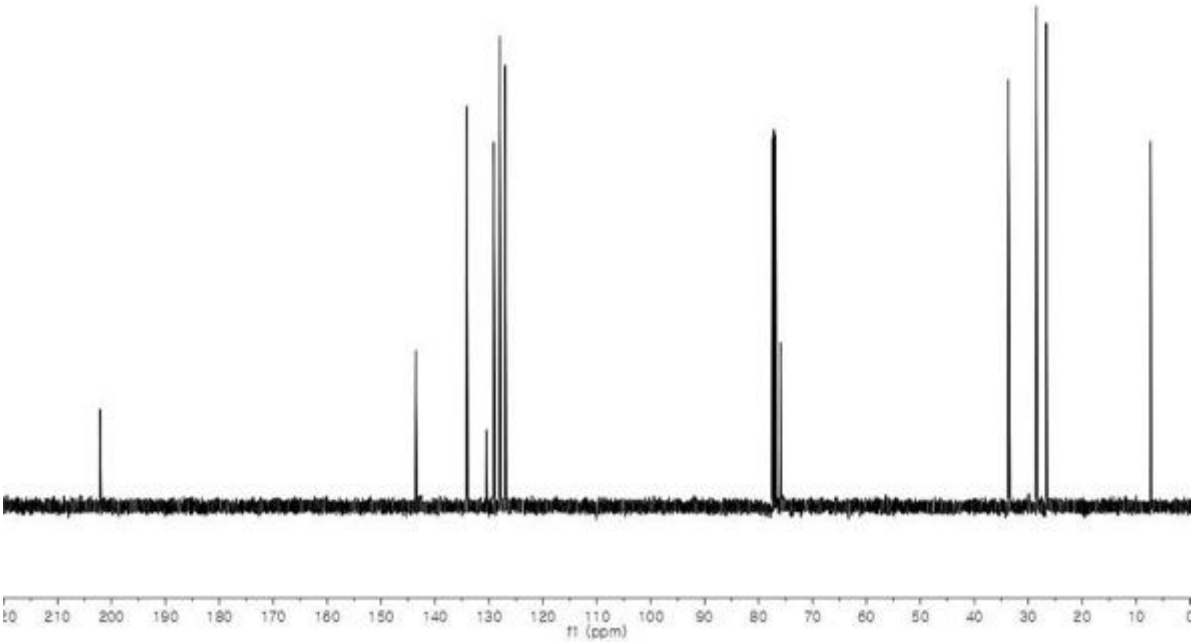
^{1}H NMR (400 MHz, CDCl): δ 8.01 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.27–7.21 (m, 1H), 3.81 (s, 1H), 3.15–2.94 (m, 2H), 2.34 (ddd, *J* = 13.5, 5.1, 2.3 Hz, 1H), 2.21–2.10 (m, 1H), 1.78–1.60 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 143.6, 134.1, 130.4, 129.1, 128.0, 127.0, 75.9, 33.7, 28.5, 26.6, 7.3 ppm.

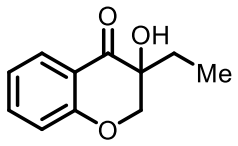
LRMS (ESI) Calcd. for $C_{12}H_{14}O_2$, $[M+Na]^+$: 213, Found: 213

FTIR (neat): 3488, 2931, 1681.


f1 (ppm)


f1 (ppm)

3-Ethyl-3-hydroxychroman-4-one (3.3m).



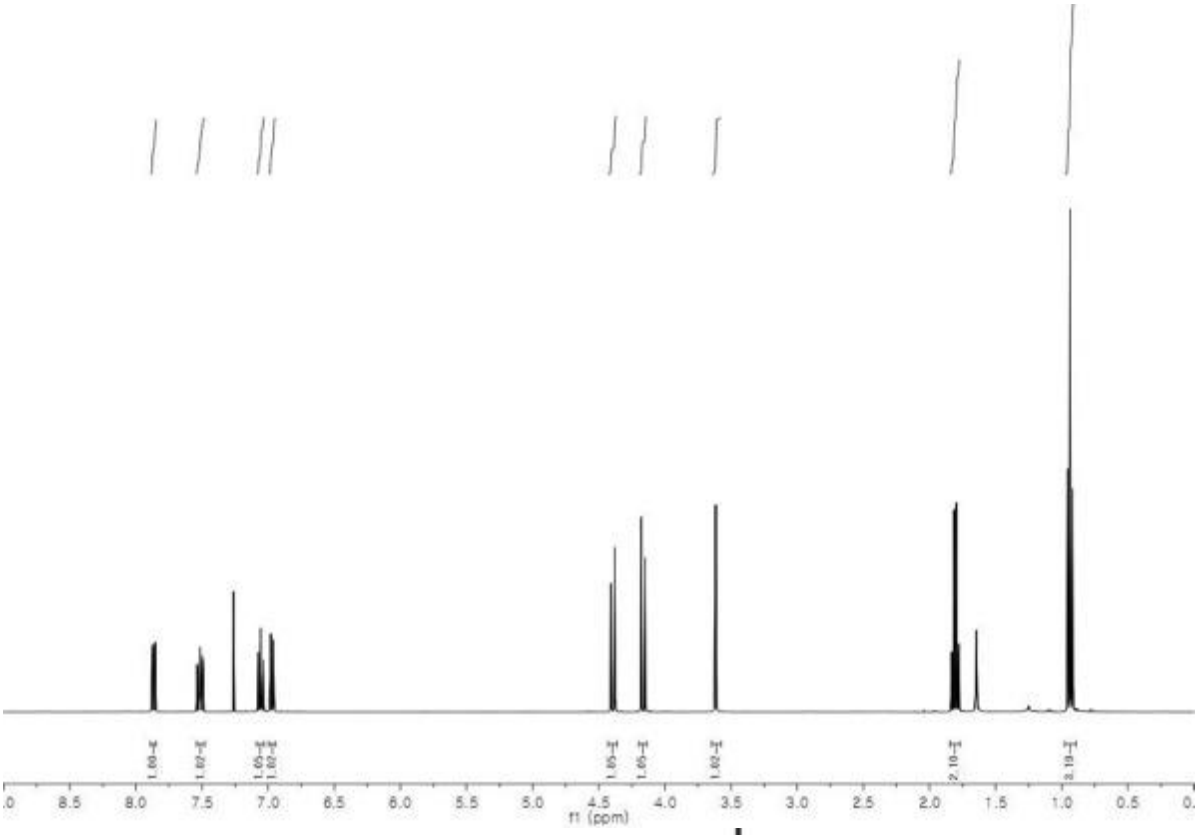
(Using ketol) In accordance with Procedure A, **3.1m** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 48 hour period. Flash column chromatography (SiO_2: 2-4% ethyl acetate/hexanes) provided the title compound (49.6 mg, 0.26 mmol) as a yellow oil in 86% yield. **(Using diol)** In accordance with Procedure A, H_2-**3.1m** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 125 mm pressure tube, 0.71 mmol, 480 mol%) in toluene (1.5 M) at 140 °C for a 48 hour period. Flash column chromatography (SiO_2: 2-4% ethyl acetate/hexanes) provided the title compound (17.3 mg, 0.09 mmol) as a yellow oil in 60% yield. NOTE: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol%), XPhos (8.5 mg, 0.018 mmol, 12 mol%) and $AdCO_2H$ (2.7 mg, 0.015mmol, 10 mol%).

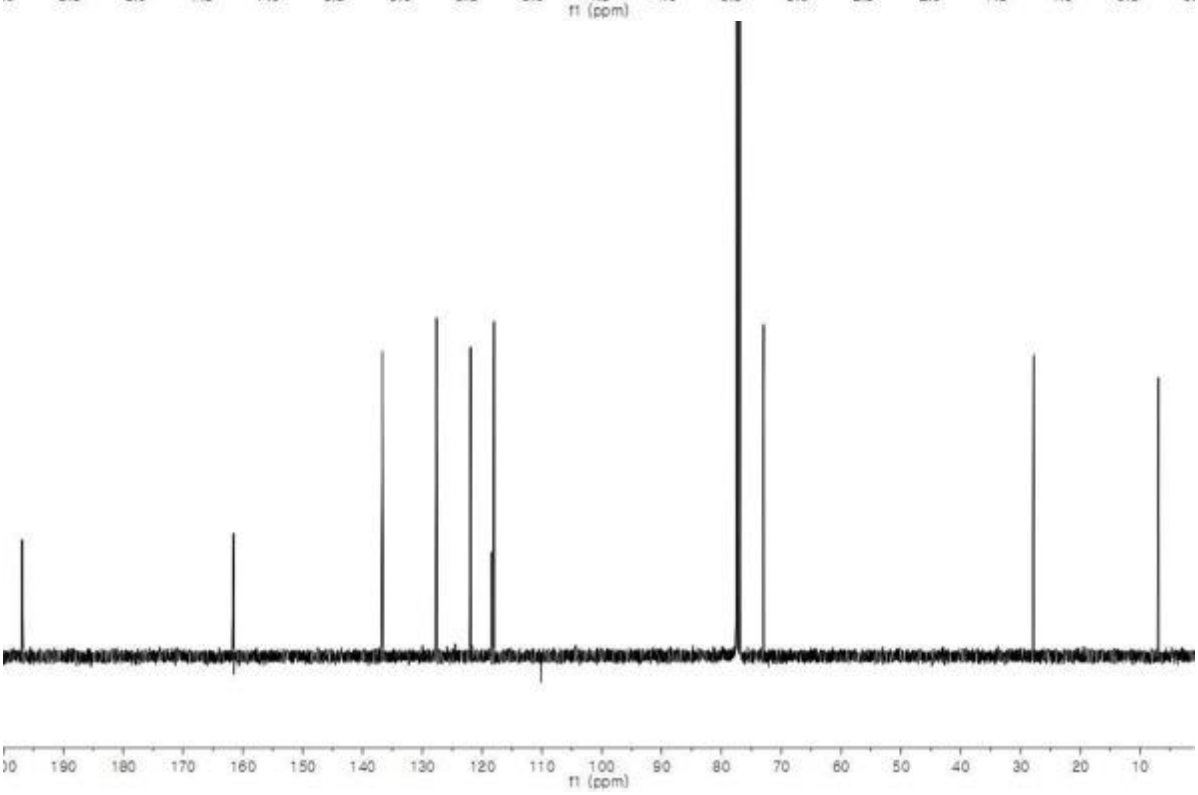
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.85 (m, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 1.8 Hz, 1H), 7.06 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 6.97 (dd, *J* = 8.4, 0.6 Hz, 1H), 4.39 (d, *J* = 11.3 Hz, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 3.62 (s, 1H), 1.80 (q, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 161.5, 136.7, 127.6, 121.9, 118.5, 118.0, 73.1, 72.9, 27.8, 7.0 ppm.

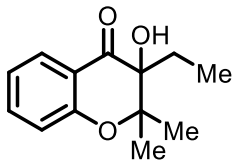
LRMS (CI) Calcd. for $C_{11}H_{12}O_3$, $[M+H]^+$: 193, Found: 193

FTIR (neat): 3466, 2973, 2936, 1691, 1607.


1.00
1.02
1.05
1.02
1.05
1.05
1.02
2.10
3.19
f1 (ppm)


f1 (ppm)

3-Ethyl-3-hydroxy-2,2-dimethylchroman-4-one (3.3n).



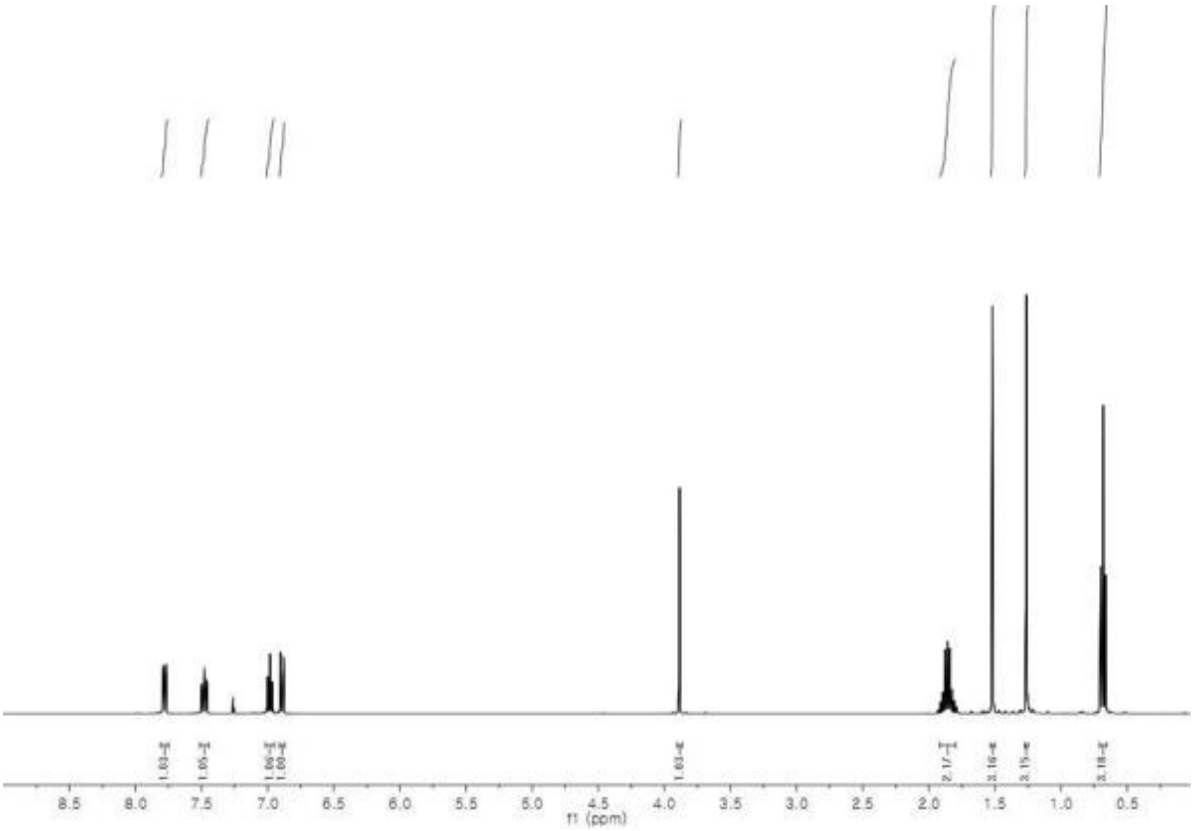
(Using ketol) In accordance with Procedure A, **3.1n** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 140 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 2-4% ether/hexanes) provided the title compound (56.2 mg, 0.26 mmol) as a yellow oil in 85% yield. **(Using diol)** In accordance with Procedure A, H_2-**3.1n** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 390 mol%) in toluene (1.5 M) at 140 ^{o}C for a 48 hour period. Flash column chromatography (SiO_2: 2-4% ethyl acetate/hexanes) provided the title compound (31.1 mg, 0.14 mmol) as a yellow oil in 94% yield. NOTE: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol%), XPhos (8.5 mg, 0.018 mmol, 12 mol%).

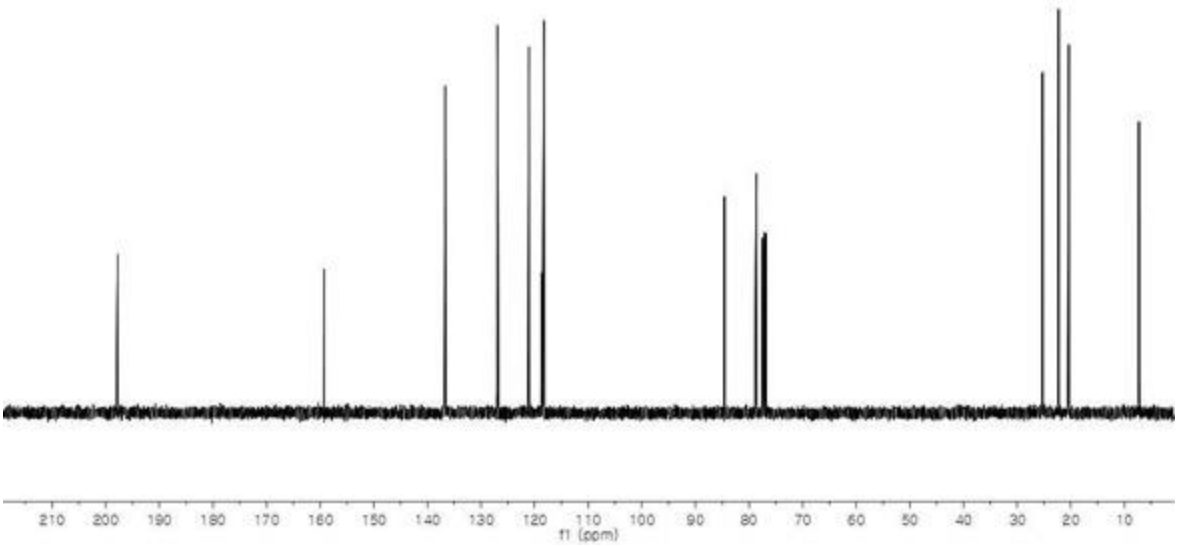
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (ddd, *J* = 8.6, 7.2, 1.8 Hz, 1H), 6.98 (dt, *J* = 12.0, 2.5 Hz, 1H), 6.89 (dd, *J* = 8.4, 0.5 Hz, 1H), 3.89 (s, 1H), 1.92–1.80 (m, 2H), 1.52 (s, 3H), 1.26 (s, 3H), 0.68 (t, *J* = 7.5 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 159.3, 136.7, 126.9, 121.1, 118.7, 118.3, 84.6, 78.7, 25.3, 22.2, 20.4, 7.3 ppm.

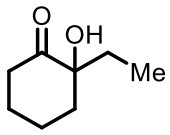
LRMS (ESI) Calcd. for $C_{13}H_{16}O_3$, $[M+Na]^+$: 243, Found: 243

FTIR (neat): 3484, 2976, 1690.


1.03
1.05
1.00
1.03
1.03
2.17
3.16
3.15
3.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-Ethyl-2-hydroxycyclohexan-1-one (3.3o).



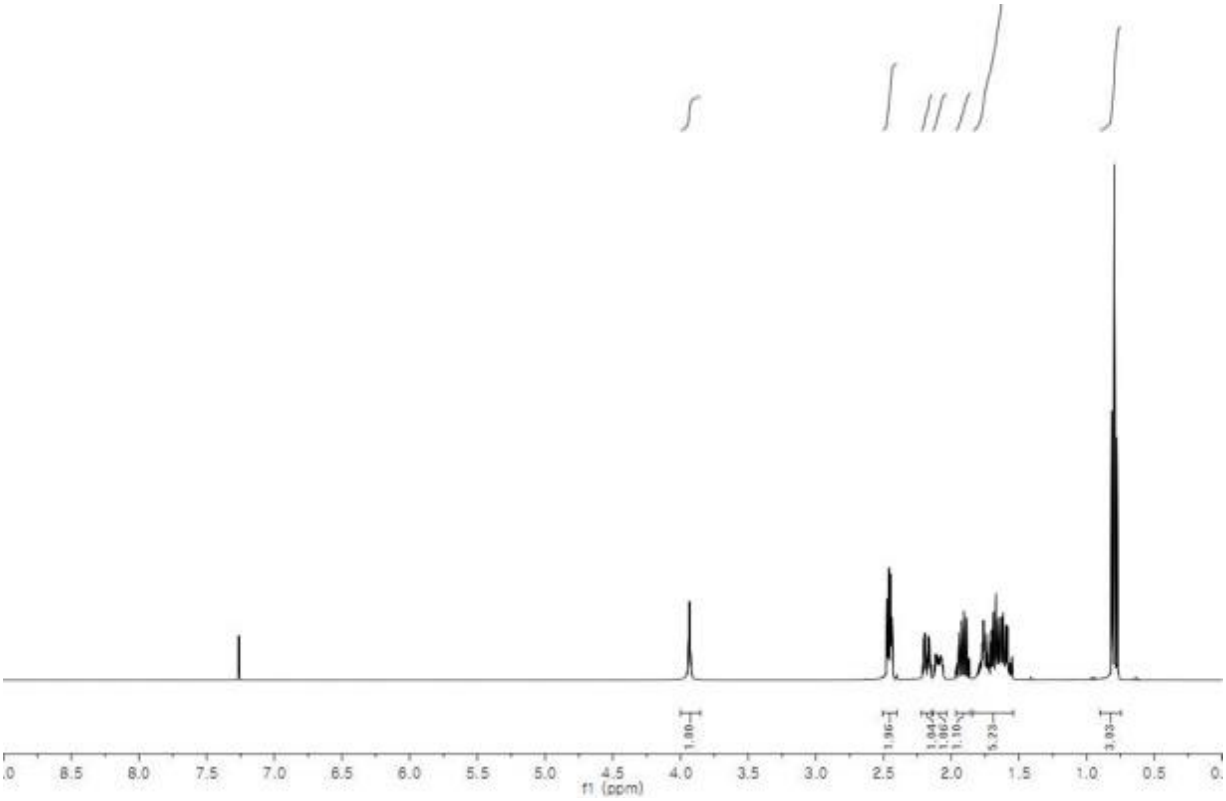
(Using ketol) In accordance with Procedure A, **3.1o** (0.3 mmol, 100 mol%) was reacted with ethylene (15 x 100 mm pressure tube, 0.58 mmol, 190 mol%) in toluene (2.0 M) at 130 °C for a 48 hour period. Flash column chromatography (SiO_2: 5-10% ether/hexanes) provided the title compound (31.1 mg, 0.22 mmol) as a colorless oil in 73% yield. **(Using diol)** In accordance with Procedure A, H_2-**3.1o** (0.15 mmol, 100 mol%) was reacted with ethylene (15 x 125 mm pressure tube, 0.71 mmol, 480 mol%) in meistylene (2.0 M) at 150 °C for a 48 hour period. Flash column chromatography (SiO_2: 5-10% ether/hexanes) provided the title compound (10.7 mg, 0.15 mmol) as a colorless oil in 50% yield. NOTE: $Os_3(CO)_{12}$ (4.1 mg, 0.0045 mmol, 3 mol%), XPhos (13.2 mg, 0.027 mmol, 18 mol%) and $AdCO_2H$ (4.1 mg, 0.023 mmol, 15 mol%).

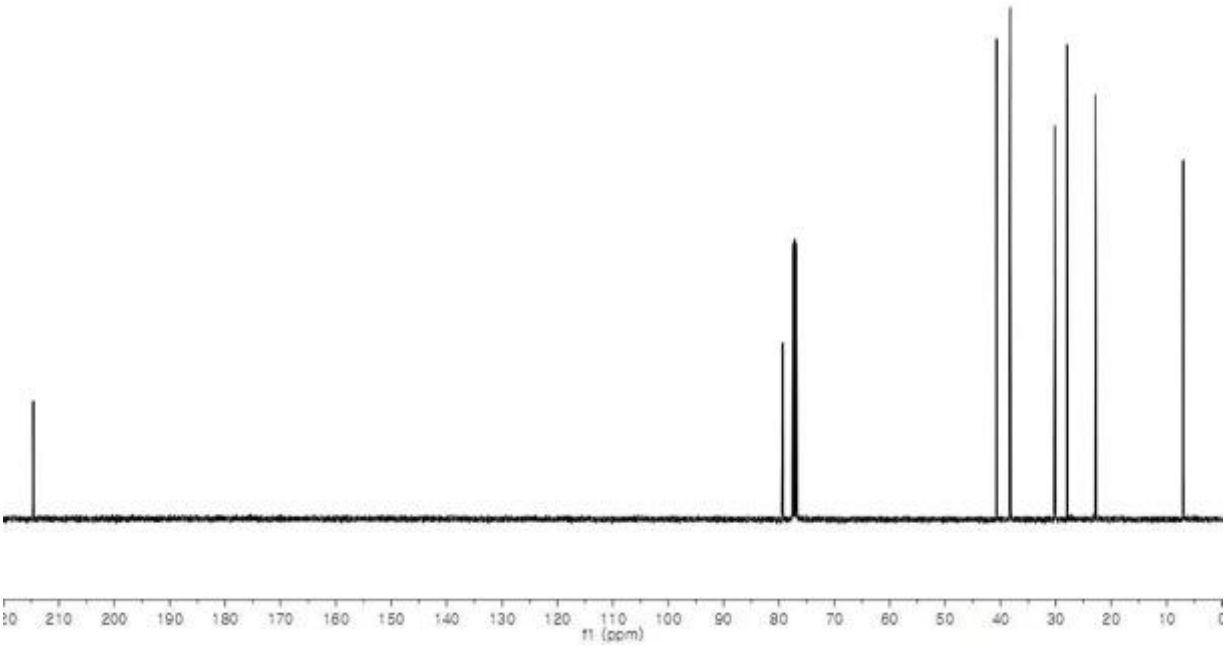
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 1H), 2.51–2.40 (m, 2H), 2.18 (ddd, *J* = 13.1, 5.8, 3.0 Hz, 1H), 2.14–2.03 (m, 1H), 1.91 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.84–1.54 (m, 5H), 0.90–0.75 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 214.6, 79.4, 40.7, 38.2, 30.2, 28.0, 22.9, 7.0 ppm

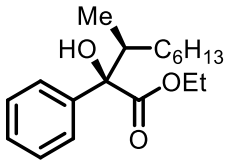
LRMS (ESI) Calcd. for $C_8H_{14}O_2$, $[M+Na]^+$: 165, Found: 165

FTIR (neat): 3485, 2938, 1707.


1.80
1.96
1.04
1.00
1.10
5.23
3.83
f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-3-methyl-2-phenylnonanoate (3.4a).



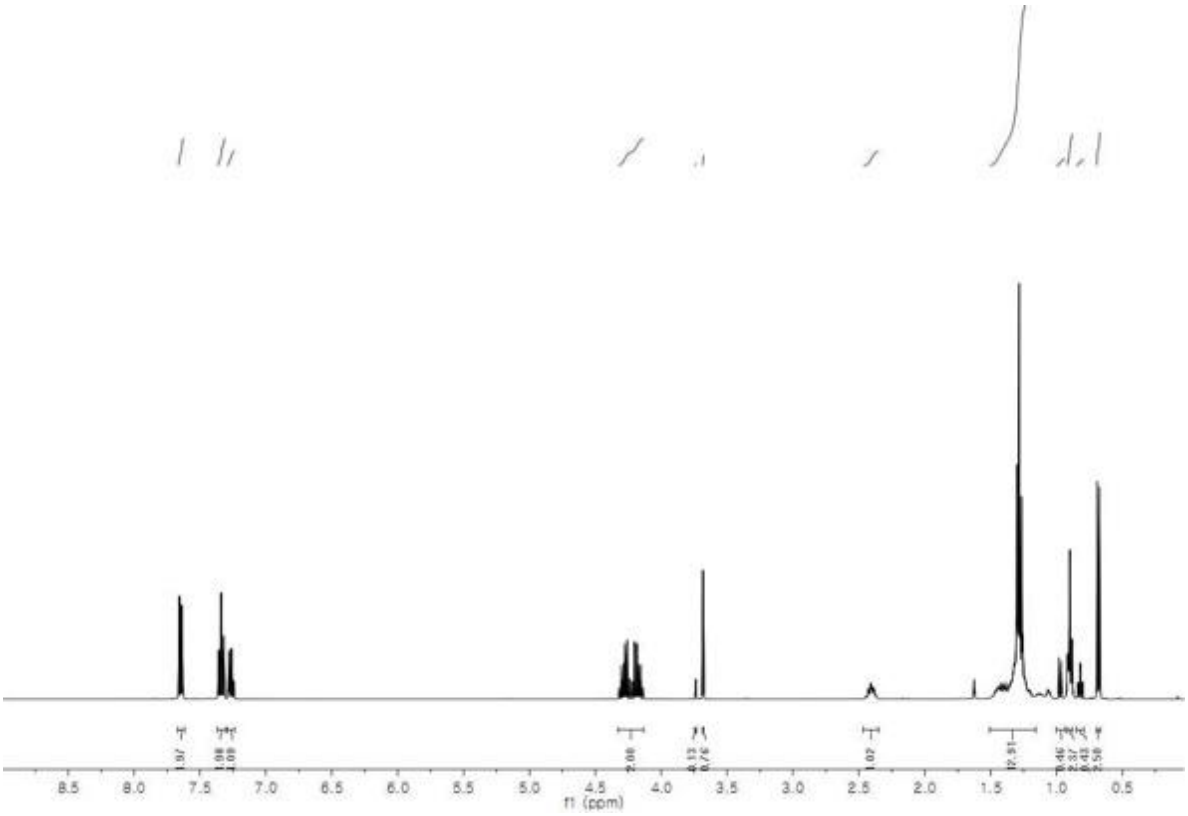
In accordance with Procedure B, **3.1a** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2% ether/hexanes) provided the title compound (31.1 mg, 0.22 mmol, *d.r.* = 5:1) as a colorless oil in 62% yield.

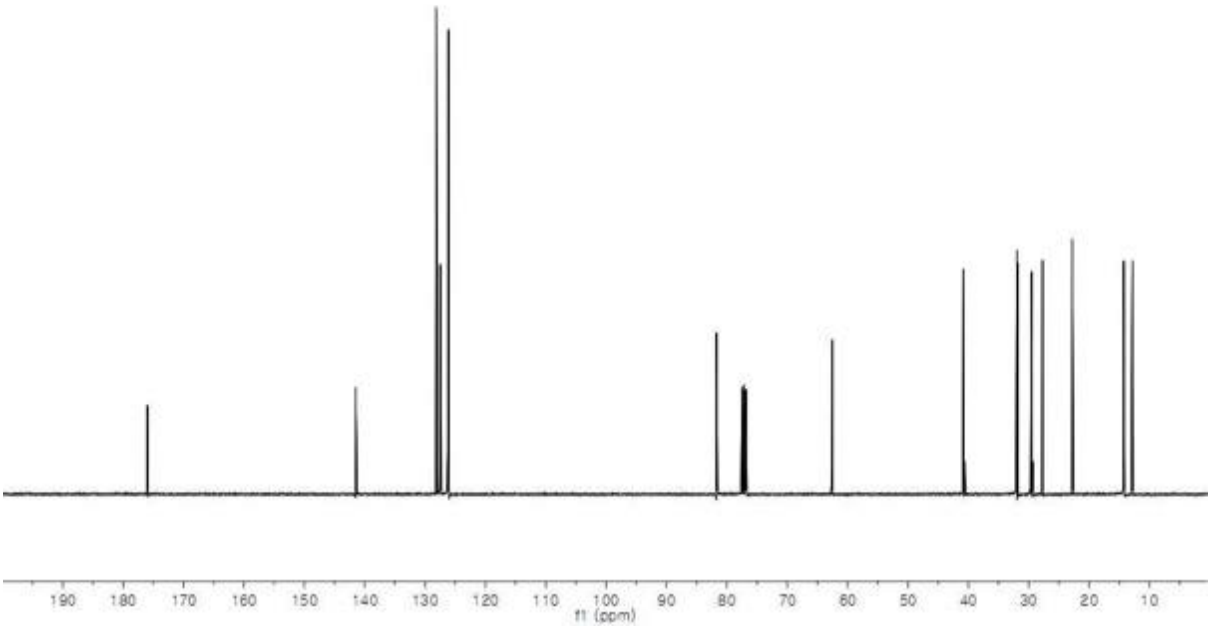
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.67–7.62 (m, 2H), 7.37–7.30 (m, 2H), 7.29–7.24 (m, 1H), 4.33–4.13 (m, 2H), 3.68 (d, *J* = 0.6 Hz, 1H), 2.47–2.35 (m, 1H), 1.51–1.16 (m, 13H), 0.90 (dd, *J* = 8.9, 4.9 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H). (minor) 7.67–7.62 (m, 2H), 7.37–7.30 (m, 2H), 7.29–7.24 (m, 1H), 4.33–4.13 (m, 2H), 3.74 (d, *J* = 0.6 Hz, 1H), 2.47–2.35 (m, 1H), 1.51–1.16 (m, 13H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 176.0, 141.5, 128.1, 127.5, 126.1, 81.7, 62.5, 40.8, 31.9, 31.8, 29.5, 27.7, 22.8, 14.3, 14.2, 12.8. (minor) 175.9, 141.3, 128.1, 127.5, 126.2, 81.6, 62.6, 40.6, 31.9, 29.6, 29.3, 27.6, 22.7, 14.2, 14.1, 12.8 ppm.

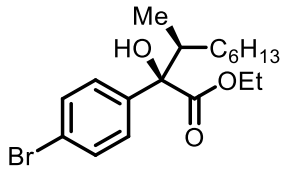
LRMS (ESI) Calcd. for $C_{18}H_{28}O_3$, $[M+Na]^+$: 315, Found: 315

FTIR (neat): 3514, 2928, 2857, 1721.


1.97
1.98
1.00
2.08
0.13
0.76
1.07
12.51
2.46
2.37
0.43
0.50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-(4-bromophenyl)-2-hydroxy-3-methylnonanoate (3.4b).



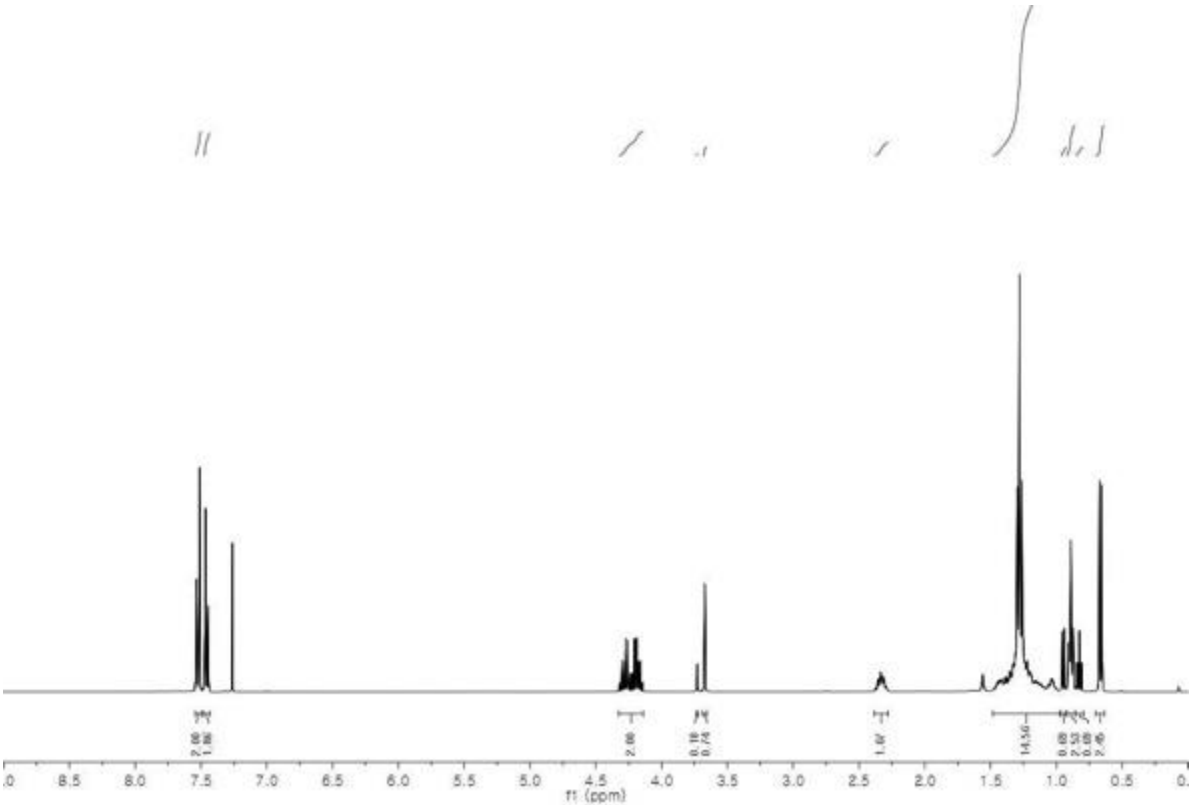
In accordance with Procedure B, **3.1b** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 20-35% dichloromethane/hexanes) provided the title compound (45.4 mg, 0.12 mmol, *d.r.* = 4:1) as a colorless oil in 61% yield.

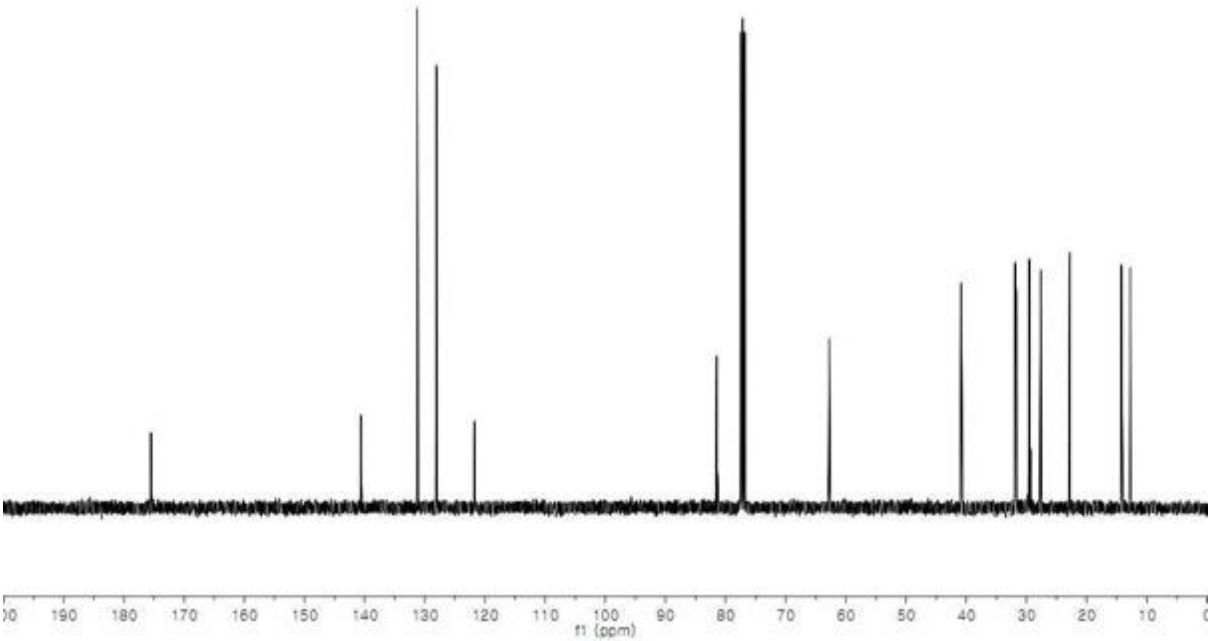
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.54–7.50 (m, 2H), 7.48–7.43 (m, 2H), 4.33–4.14 (m, 2H), 3.67 (s, 1H), 2.38–2.28 (m, 1H), 1.48–0.97 (m, 13H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H). (minor) 7.54–7.50 (m, 2H), 7.48–7.43 (m, 2H), 4.33–4.14 (m, 2H), 3.73 (s, 1H), 2.38–2.28 (m, 1H), 1.48–0.97 (m, 13H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.5, 140.6, 131.3, 128.1, 121.7, 81.5, 62.8, 40.9, 31.9, 31.7, 29.5, 27.6, 22.8, 14.3, 14.2, 12.8. (minor) 175.4, 140.6, 131.3, 128.1, 121.7, 81.4, 62.9, 40.7, 31.9, 29.6, 29.3, 27.6, 22.7, 14.2, 14.1, 12.8 ppm.

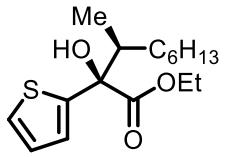
LRMS (ESI) Calcd. for $C_{18}H_{27}BrO_3$, $[M+Na]^+$: 393, Found: 393

FTIR (neat): 3507, 2927, 2856, 1723.


f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-3-methyl-2-(thiophen-2-yl)nonanoate (3.4i).



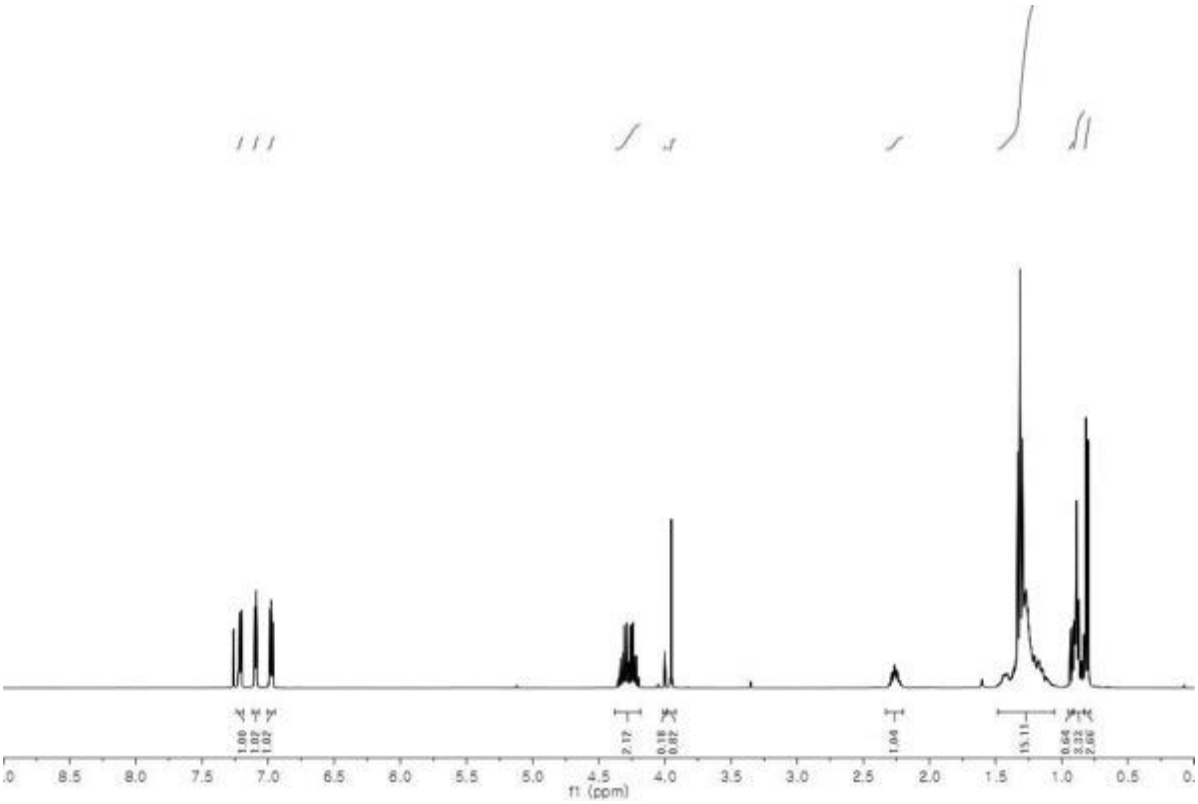
In accordance with Procedure B, **3.1i** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 ºC for a 40 hour period. Flash column chromatography (SiO_2: 20-40% dichloromethane/hexanes) provided the title compound (47.8 mg, 0.16 mmol, *d.r.* = 5:1) as a colorless oil in 80% yield.

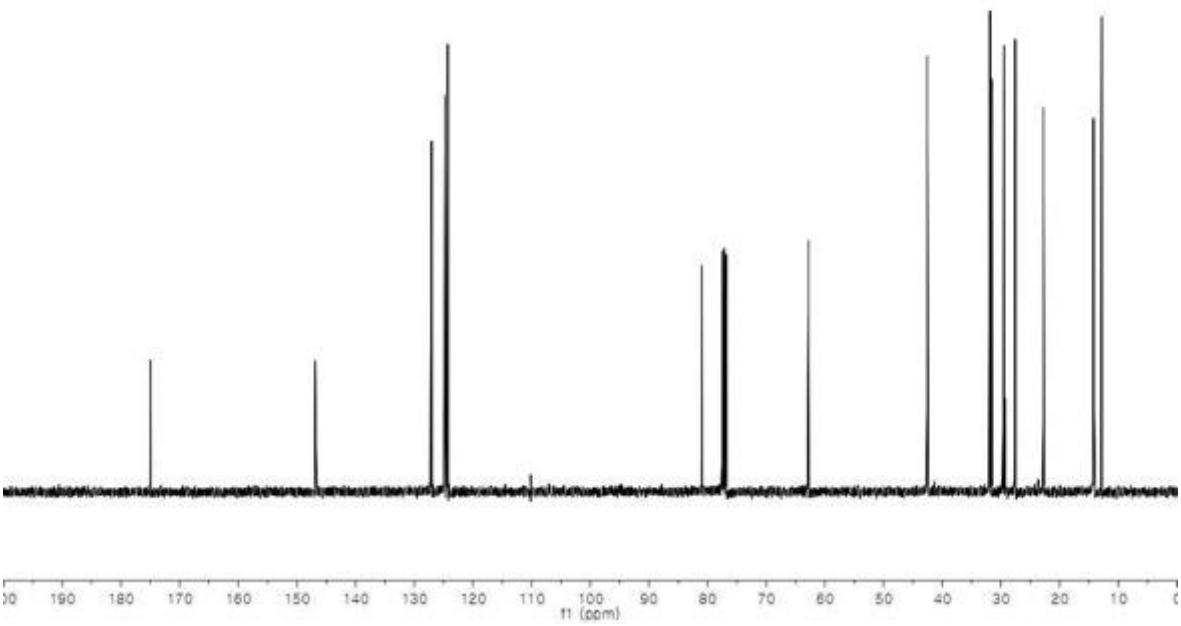
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.21 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.38–4.19 (m, 2H), 3.95 (d, *J* = 0.5 Hz, 1H), 2.33–2.20 (m, 1H), 1.48–1.05 (m, 14H), 0.91–0.83 (m, 2H), 0.81 (d, *J* = 6.8 Hz, 3H). (minor) 7.22 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.99–6.97 (m, 1H), 4.38–4.19 (m, 2H), 4.00 (d, *J* = 0.5 Hz, 1H), 2.33–2.20 (m, 1H), 1.48–1.05 (m, 14H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.91–0.83 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.0, 146.9, 127.1, 124.8, 124.3, 81.0, 62.8, 42.6, 31.9, 31.6, 29.5, 27.6, 22.8, 14.22, 14.15, 12.8. (minor) 174.9, 146.7, 127.1, 124.9, 124.4, 80.9, 62.9, 42.5, 31.9, 29.6, 29.4, 27.7, 22.7, 14.2, 14.0, 12.8 ppm.

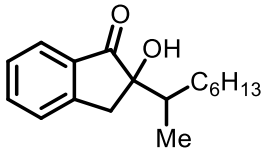
LRMS (ESI) Calcd. for $C_{16}H_{26}O_3S$, $[M+Na]^+$: 321, Found: 321

FTIR (neat): 3502, 2929, 2857, 1725.


1.00
1.02
1.02
2.17
0.18
0.82
1.04
15.11
0.64
3.32
2.00
f1 (ppm)


f1 (ppm)

2-Hydroxy-2-(octan-2-yl)-2,3-dihydro-1H-inden-1-one (3.4j).



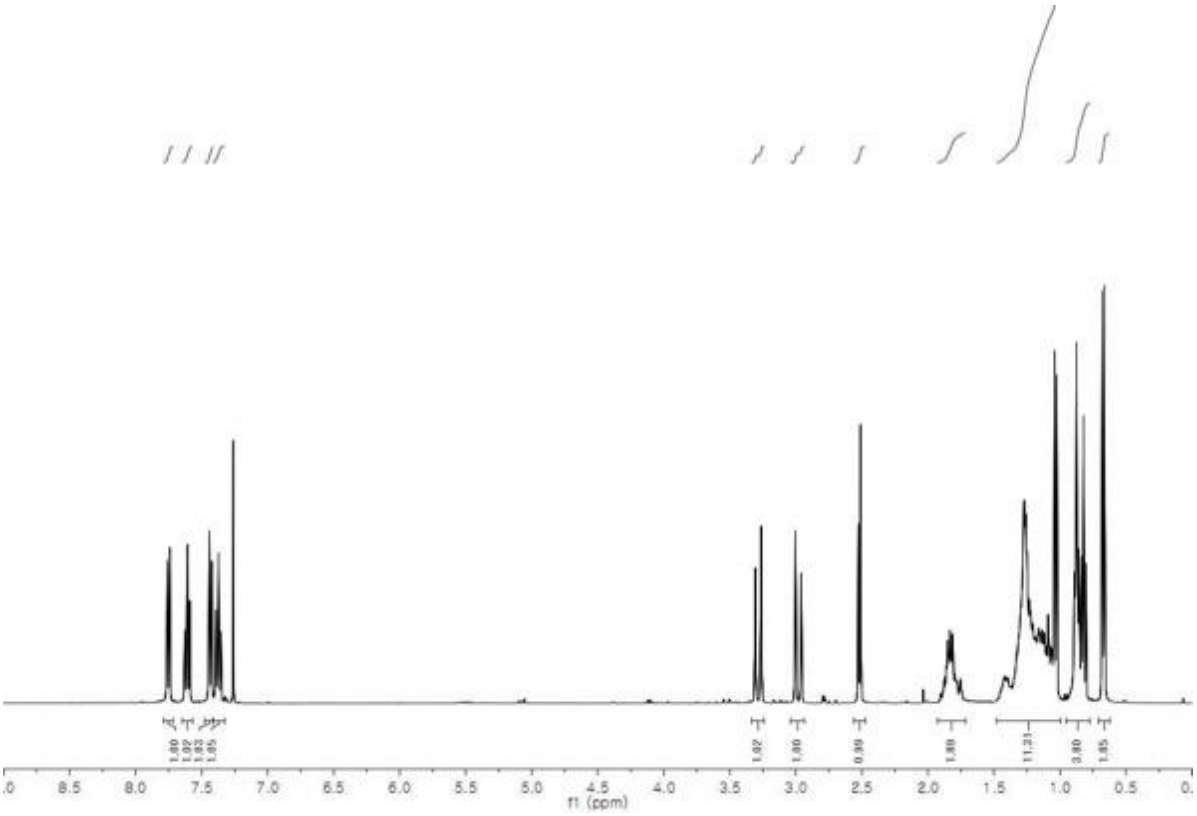
In accordance with Procedure B, **3.1j** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 °C for a 40 hour period. Flash column chromatography (SiO_2: 2-3% ether/hexanes) provided the title compound (44.3 mg, 0.17 mmol, *d.r.* = 1:1) as a colorless oil in 85% yield.

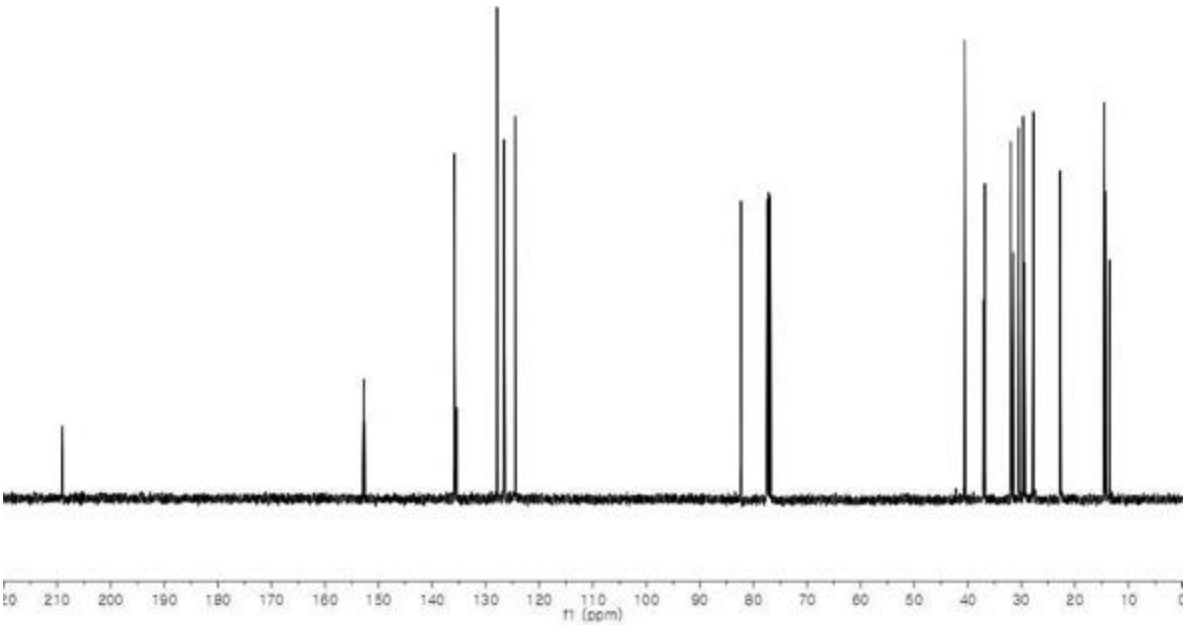
^{1}H NMR (400 MHz, $CDCl_3$): δ (A) 7.75 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.37 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.28 (d, *J* = 17.4 Hz, 1H), 2.98 (d, *J* = 17.4 Hz, 1H), 2.51 (s, 1H), 1.93–1.72 (m, 15H), 1.48–0.99 (m, 9.5H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.67 (d, *J* = 6.9 Hz, 3H). (B) 7.75 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.37 (dd, *J* = 7.5 Hz, 7.5 Hz, 1H), 3.28 (d, *J* = 17.4 Hz, 1H), 2.98 (d, *J* = 17.4 Hz, 1H), 2.53 (s, 1H), 1.93–1.72 (m, 1.5 H), 1.48–0.99 (m, 12.5H), 0.82 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 209.1, 152.8, 135.8, 135.4, 127.8, 126.6, 124.5, 82.3, 40.6, 36.8, 32.0, 30.5, 29.6, 27.8, 22.8, 14.5, 13.5. (B) 209.0, 152.6, 135.8, 135.5, 127.8, 126.7, 124.5, 82.3, 40.6, 37.1, 31.9, 31.5, 29.4, 27.7, 22.7, 14.22, 14.16 ppm.

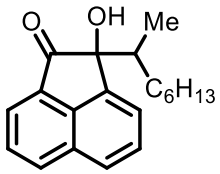
LRMS (ESI) Calcd. for $C_{17}H_{24}O_2$, $[M+Na]^+$: 283, Found: 283

FTIR (neat): 3447, 2926, 1709.


1.00
1.02
1.03
1.05
1.02
1.00
0.99
1.89
11.31
3.80
1.85
f1 (ppm)


f1 (ppm)

2-Hydroxy-2-(octan-2-yl)acenaphthylen-1(2H)-one (3.4k).



(Using dihydro-3.1k) In accordance with Procedure B, *dihydro*-**3.1k** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (41.5 mg, 0.14 mmol, *d.r.* = 2:1) as a light green solid in 70% yield. **(Using 3.1k)** In accordance with Procedure B, **3.1k** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (56.3 mg, 0.19 mmol, *d.r.* = 2:1) as a light green solid in 95% yield. **(Using dehydro-3.1k)** In accordance with Procedure B, *dehydro*-**3.1k** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (40.3 mg, 0.14 mmol, *d.r.* = 2:1) as a light green solid in 68% yield. NOTE: The reaction was conducted in the presence of 1,3-butane diol (36.0 mg, 0.4 mmol, 200 mol%).

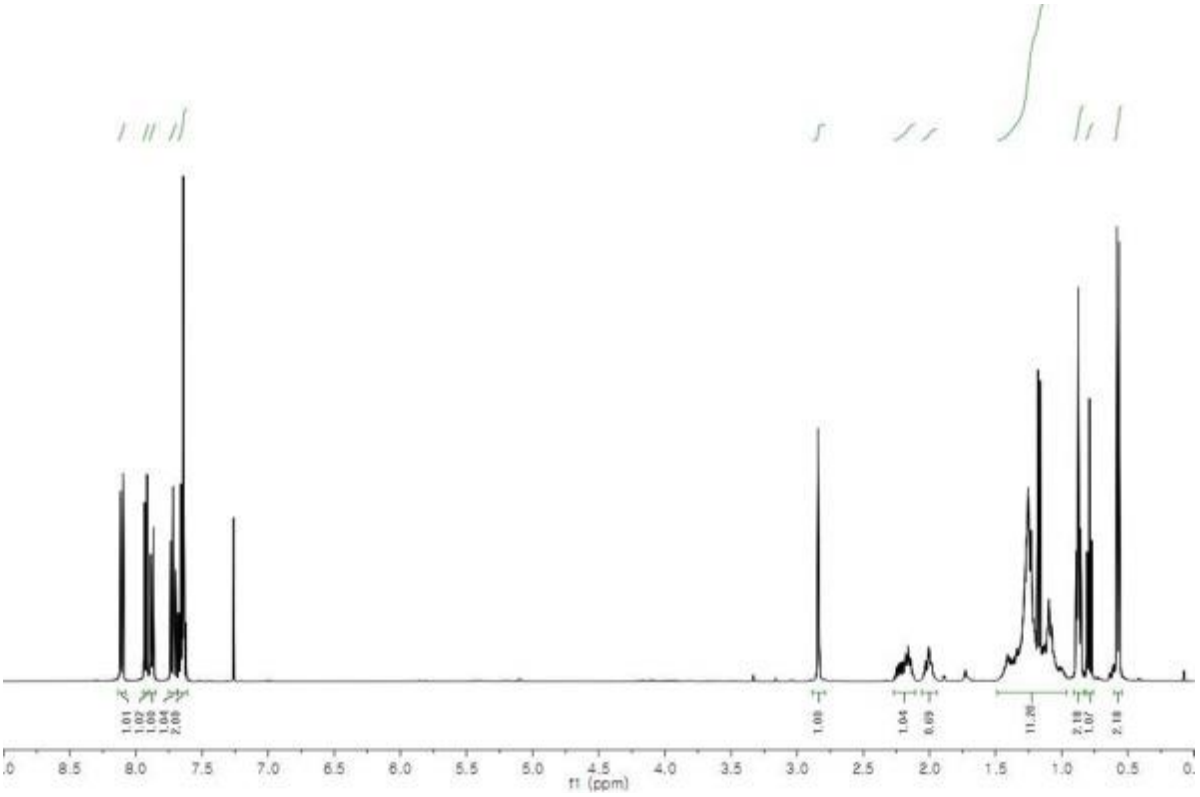
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 8.11 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.92 (ddd, *J* = 4.0, 2.0, 2.0 Hz, 1H), 7.90–7.85 (m, 1H), 7.72 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.68–7.61 (m, 2H), 2.84 (d, *J* = 2.4 Hz, 1H), 2.27–1.94 (m, 1H), 1.49–0.96 (m, 10H), 0.91–0.83 (m, 3H), 0.58 (t, *J* = 6.2 Hz, 3H). (minor) 8.11 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.92 (ddd, *J* = 4.0, 2.0, 2.0 Hz, 1H), 7.90–7.85 (m, 1H), 7.72 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.68–7.61 (m, 2H), 2.84 (d, *J* = 2.4 Hz, 1H), 2.27–1.94 (m, 1H), 1.49–0.96 (m, 13H), 0.79 (t, *J* = 7.1 Hz, 3H) ppm.

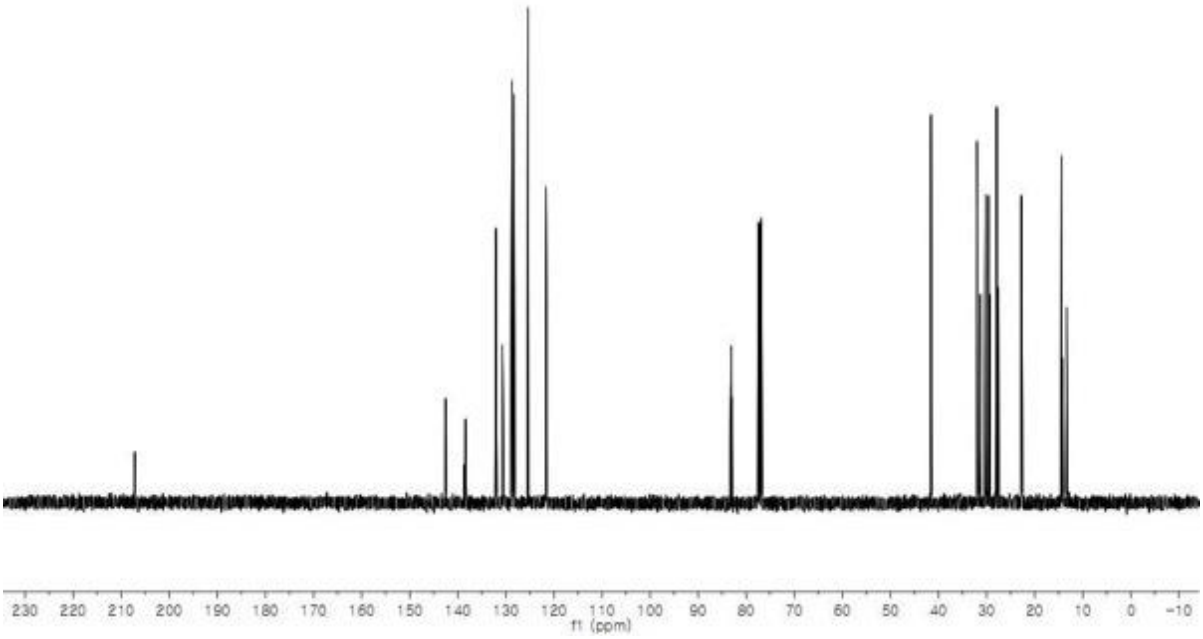
^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 207.2, 142.5, 138.4, 132.01, 131.99, 130.7, 128.7, 128.3, 125.4, 121.7, 121.6, 83.1, 41.6, 32.0, 30.2, 29.6, 27.9, 22.8, 14.4, 14.2. (minor) 207.2, 142.4, 138.7, 132.0, 131.9, 130.8, 128.7, 128.3, 125.4, 121.6, 121.4, 82.9, 41.4, 31.8, 31.3, 29.2, 27.5, 22.6, 14.1, 13.3 ppm.

LRMS (ESI) Calcd. for $C_{20}H_{24}O_2$, $[M+Na]^+$: 319, Found: 319

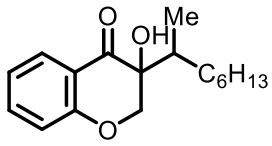
FTIR (neat): 3423, 2924, 1708

MP: 79.8–81.1 °C.


1.01
1.02
1.00
1.04
2.00
1.00
1.04
0.69
11.26
2.18
1.07
2.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3-Hydroxy-3-(octan-2-yl)chroman-4-one (3.4m).



In accordance with Procedure B, **3.1m** (0.2 mmol, 100 mol%) was reacted with 1-octene (13 x 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol%) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 2-3% ether/hexanes) provided the title compound (34.8 mg, 0.13 mmol, *d.r.* = 1:1) as a pale yellow solid in 63% yield.

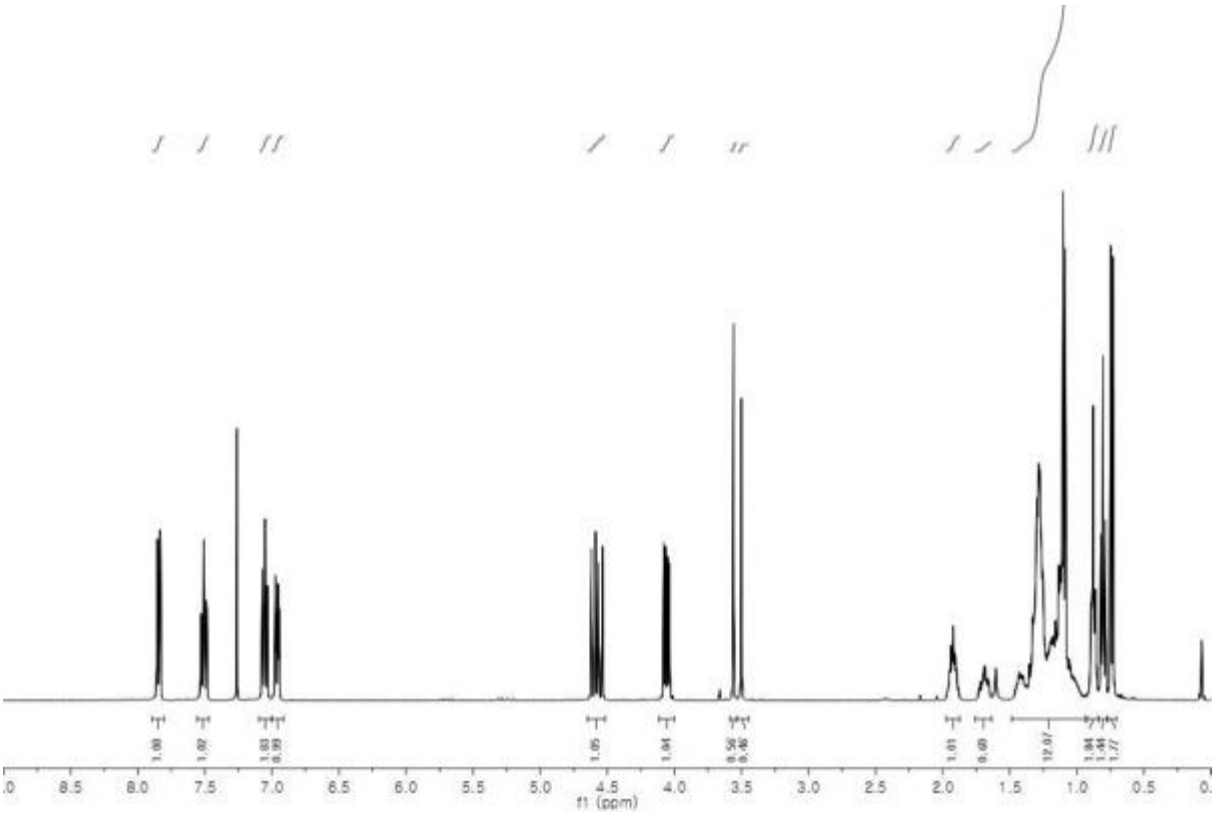
^{1}H NMR (400 MHz, $CDCl_3$): δ (A) 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56–7.47 (m, 1H), 7.05 (ddd, *J* = 8.2, 1.9, 1.0 Hz, 1H), 6.96 (ddd, *J* = 8.4, 3.0, 0.6 Hz, 1H), 4.58 (dd, *J* = 21.0, 11.7 Hz, 1H), 4.06 (dd, *J* = 11.7, 5.6 Hz, 1H), 3.56 (s, 1H), 1.97–1.87 (m, 1H), 1.76–1.64 (m, 0.5H), 1.49–0.94 (m, 12.5H), 0.88 (dd, *J* = 8.4, 5.0 Hz, 3H). (B) 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56–7.47 (m, 1H), 7.05 (ddd, *J* = 8.2, 1.9, 1.0 Hz, 1H), 6.96 (ddd, *J* = 8.4, 3.0, 0.6 Hz, 1H), 4.58 (dd, *J* = 21.0, 11.7 Hz, 1H), 1.76–1.64 (m, 0.5H), 1.49–0.94 (m, 9.5H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 6.9 Hz, 3H) ppm.

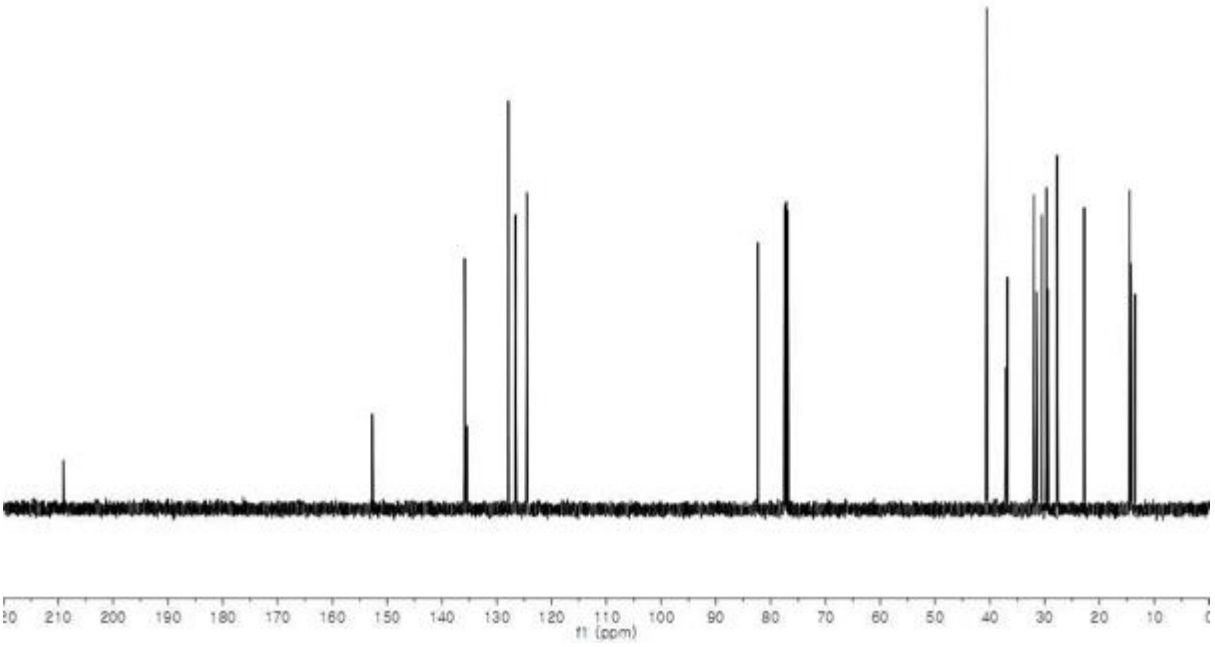
^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 209.1, 152.8, 135.8, 135.4, 127.8, 126.6, 124.5, 82.3, 40.6, 36.8, 32.0, 31.5, 29.6, 27.7, 22.8, 14.5, 14.2. (B) 209.1, 152.6, 135.8, 135.4, 127.8, 126.7, 124.5, 82.3, 40.6, 37.1, 31.9, 30.5, 29.4, 27.7, 22.7, 14.2, 13.5 ppm.

LRMS (ESI) Calcd. for $C_{17}H_{24}O_3$, $[M+Na]^+$: 299, Found: 299

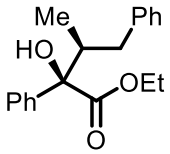
FTIR (neat): 3453, 2927, 1684

MP: 67.8–68.0 ^{o}C.


1.00
1.02
1.03
0.99
1.05
1.04
0.56
0.46
1.01
0.69
12.97
1.84
1.46
1.27
f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-3-methyl-2,4-diphenylbutanoate (3.5a).



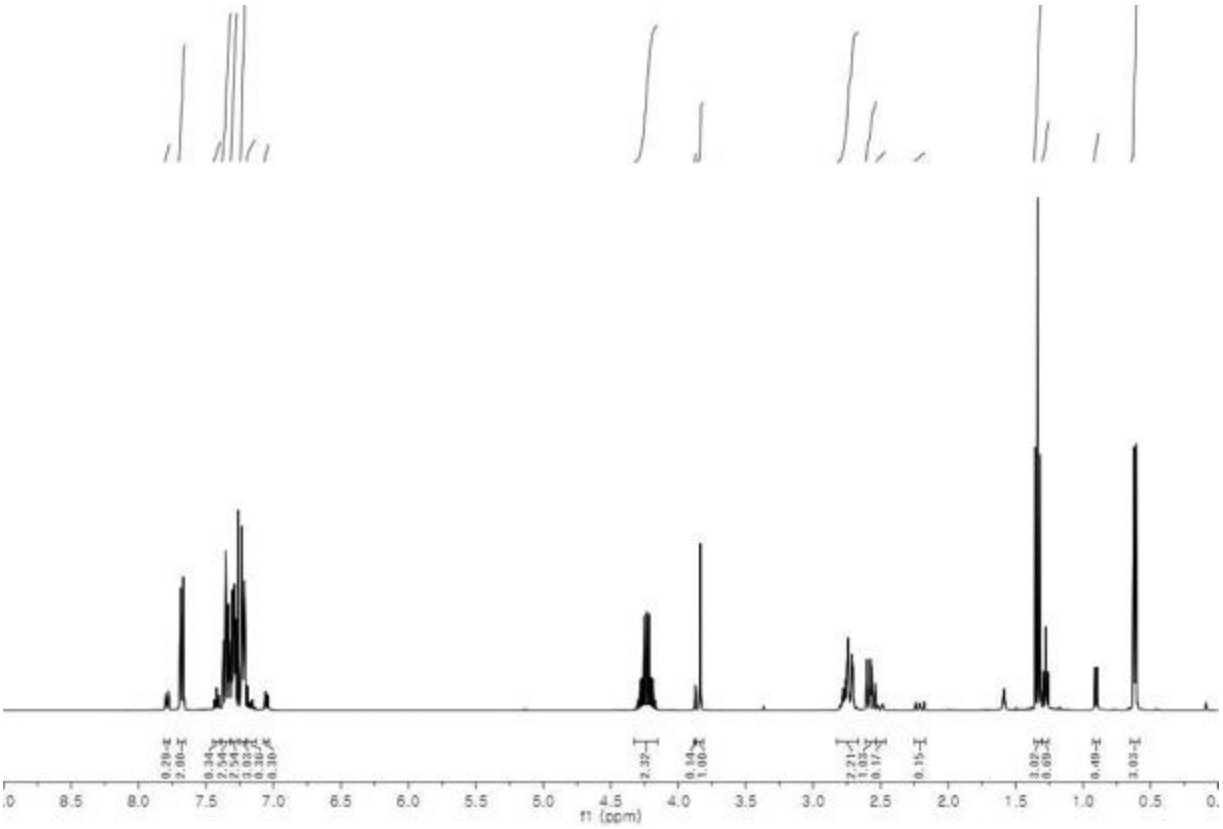
In accordance with Procedure B, **3.1a** (0.2 mmol, 100 mol%) was reacted with **3.2c** (13 x 100 mm pressure tube, 0.13 mL, 1.0 mmol, 500 mol%) in toluene (2.0 M) at 130 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 30-60% dichloromethane/hexanes) provided the title compound (34.6 mg, 0.11 mmol, *d.r.* = 5:1) as colorless oil in 58% yield. NOTE: $AdCO_2H$ (30 mol%).

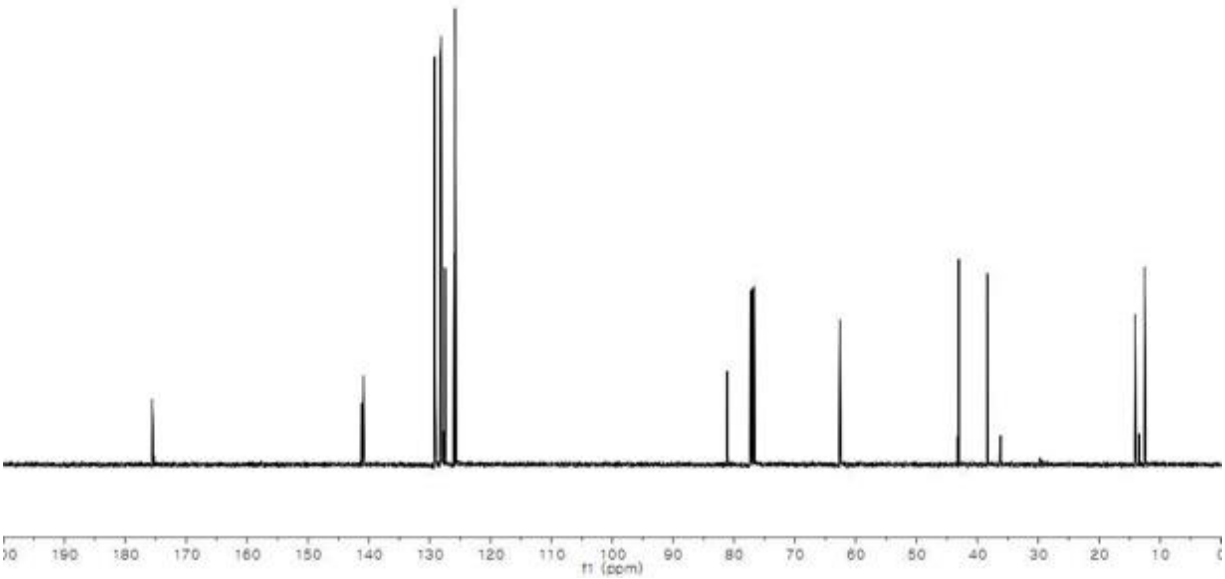
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.71–7.65 (m, 2H), 7.38–7.26 (m, 5H), 7.22 (d, *J* = 7.3 Hz, 3H), 4.33–4.15 (m, 2H), 3.84 (d, *J* = 0.5 Hz, 1H), 2.82–2.67 (m, 2H), 2.57 (dd, *J* = 13.4, 10.5 Hz 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.62 (t, *J* = 6.8 Hz, 3H). (minor) 7.81–7.77 (m, 2H), 7.42 (dd, *J* = 10.5, 4.9 Hz, 2H), 7.38–7.26 (m, 2H), 7.18 (dd, *J* = 11.2, 4.3 Hz, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 4.33–4.15 (m, 2H), 3.87 (d, *J* = 0.6 Hz, 1H), 2.82–2.67 (m, 1H), 2.50 (d, *J* = 13.7 Hz, 1H), 2.21 (dd, *J* = 13.6 Hz, 11.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.8, 141.3, 141.0, 129.4, 128.4, 128.3, 127.6, 126.1, 126.0, 81.3, 62.8, 43.2, 38.6, 14.3, 12.7. (minor) 175.5, 141.4, 141.1, 129.2, 128.4, 128.3, 127.8, 126.2, 125.9, 81.2, 62.8, 43.4, 36.4, 14.2, 13.6 ppm.

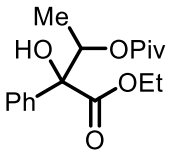
LRMS (ESI) Calcd. for $C_{19}H_{22}O_3$, $[M+Na]^+$: 321, Found: 321

FTIR (neat): 3505, 2976, 2361, 2342, 1715.


f1 (ppm)


f1 (ppm)

Ethyl 2-hydroxy-2-phenyl-3-(pivaloyloxy)butanoate (3.6a).



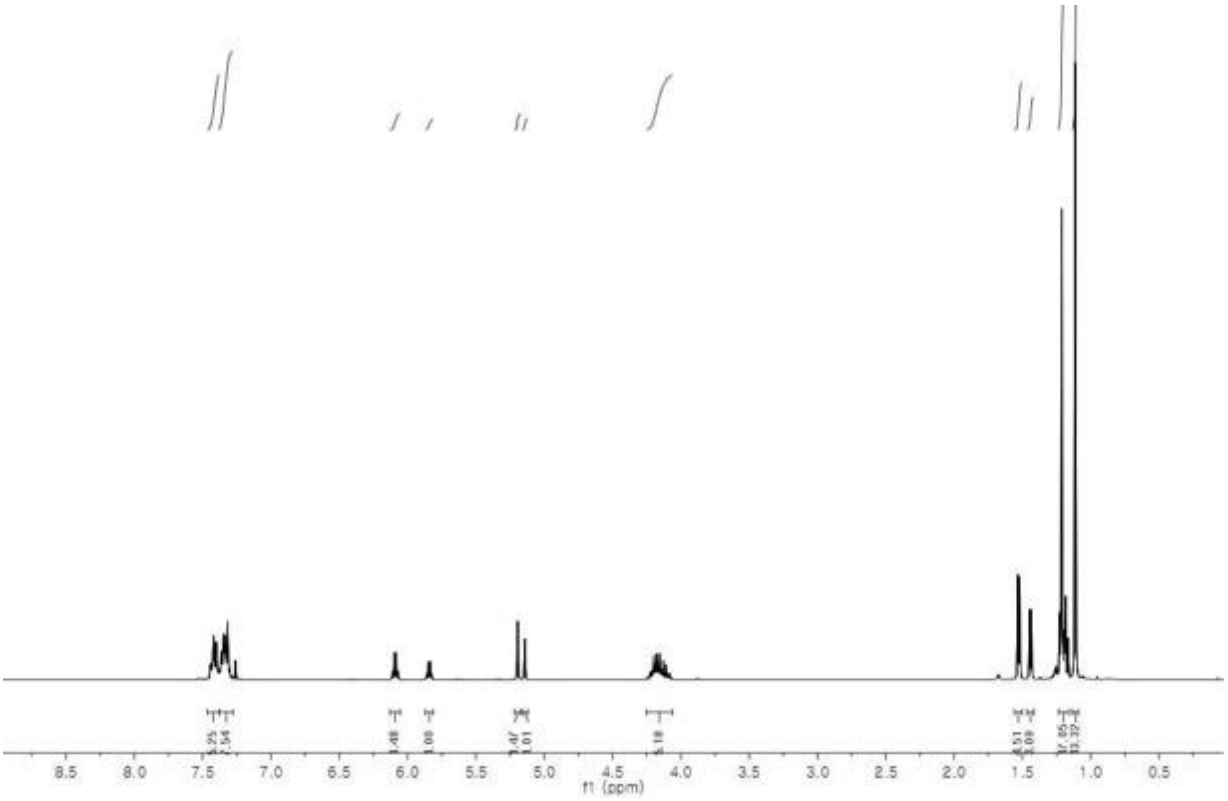
In accordance with Procedure B, **3.1a** (0.2 mmol, 100 mol%) was reacted with **3.2d** (13 x 100 mm pressure tube, 0.09 mL, 0.6 mmol, 300 mol%) in toluene (2.0 M) at 130 ^{o}C for a 24 hour period. Flash column chromatography (SiO_2: 2-4% ethyl acetate/hexanes) provided the title compound (51.8 mg, 0.25 mmol, *d.r.* = 1.5:1) as a pale yellow oil in 84% yield. NOTE: XPhos and $AdCO_2H$ was omitted.

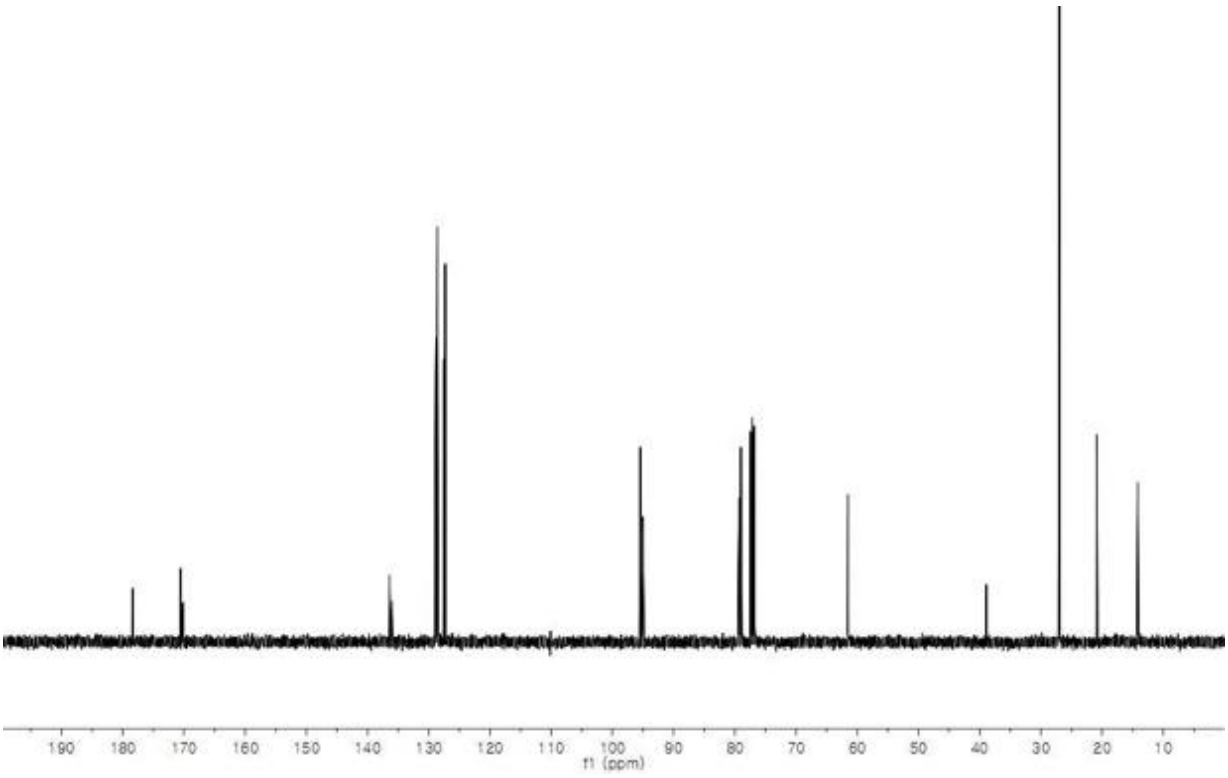
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.47–7.28 (m, 5H), 6.09 (q, *J* = 5.2 Hz, 1H), 5.19 (s, 1H), 4.25–4.06 (m, 2H), 1.53 (d, *J* = 5.2 Hz, 3H), 1.23–1.17 (m, 3H), 1.11 (s, 9H). (minor) 7.47–7.28 (m, 5H), 5.84 (q, *J* = 5.2 Hz, 1H), 5.14 (s, 1H), 4.25–4.06 (m, 2H), 1.44 (d, *J* = 5.3 Hz, 3H), 1.23–1.17 (m, 3H), 1.21 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 178.3. 170.6. 136.4. 128.7. 128.6. 127.3. 95.5. 79.0. 61.5. 38.9. 27.0. 20.9. 14.2. (minor) 178.3, 170.1, 136.0, 129.0, 128.8, 127.5, 95.0, 79.3, 61.4, 39.0, 27.1, 20.8, 14.1 ppm.

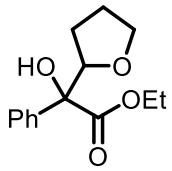
LRMS (ESI) Calcd. for $C_{17}H_{24}O_5$, $[M+Na]^+$: 331, Found: 331

FTIR (neat): 2979, 1789, 1174.


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 2-hydroxy-2-phenyl-2-(tetrahydrofuran-2-yl)acetate (3.7a).



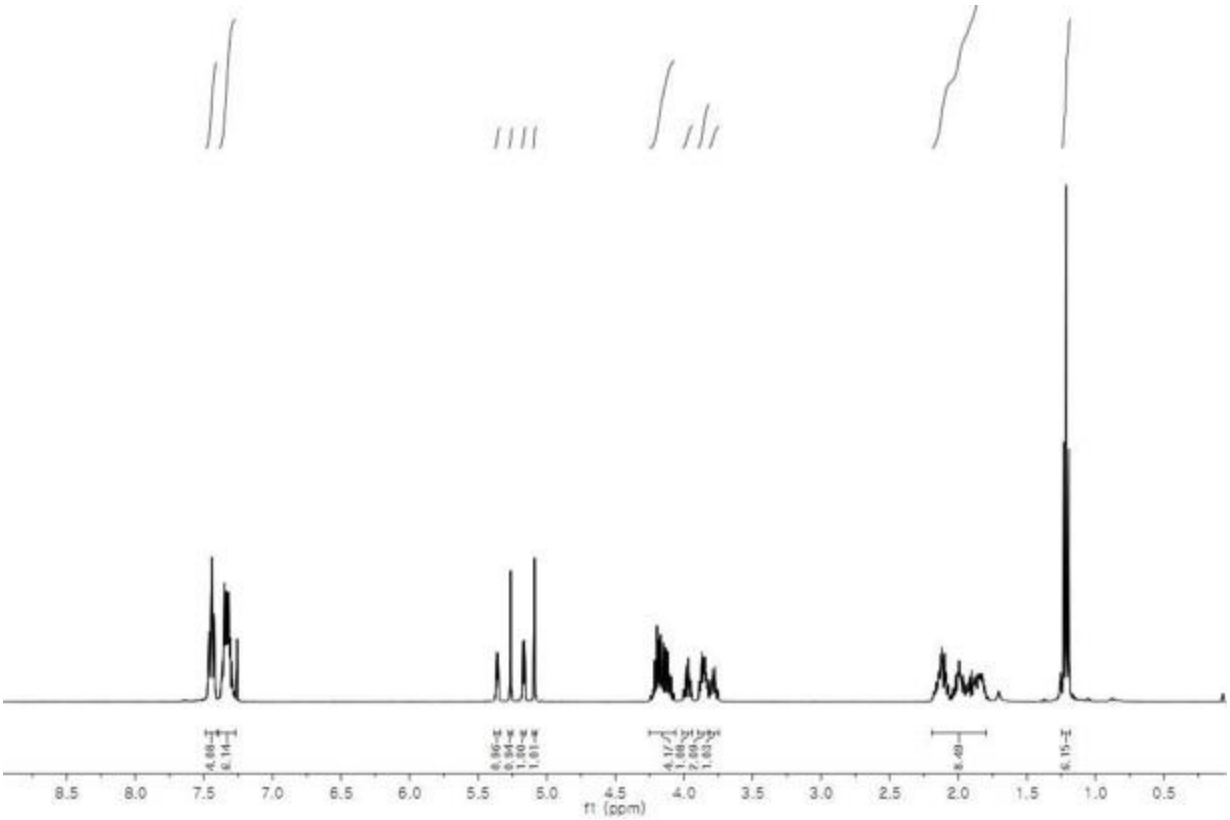
In accordance with Procedure B, **3.1a** (0.2 mmol, 100 mol%) was reacted with **3.2e** (13 x 100 mm pressure tube, 0.05 mL, 0.6 mmol, 300 mol%) in toluene (2.0 M) at 140 ºC for a 24 hour period. Flash column chromatography (SiO_2: 2-5% ethyl acetate/hexanes) provided the title compound (39.0 mg, 0.23 mmol, *d.r.* = 1:1) as a pale yellow oil in 78% yield. NOTE: XPhos and $AdCO_2H$ was omitted.

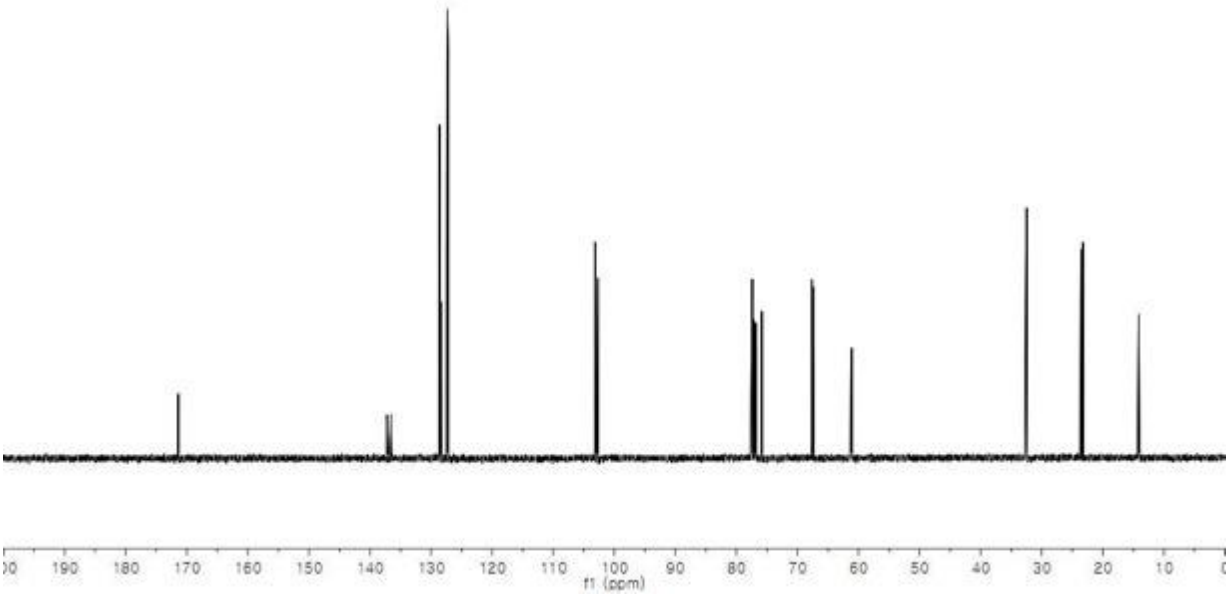
^{1}H NMR (400 MHz, $CDCl_3$): δ (A) 7.44 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 2H), 7.39–7.27 (m, 3H), 5.36 (d, *J* = 3.6 Hz, 1H), 5.26 (s, 1H), 4.25–4.06 (m, 2H), 4.01–3.94 (m, 1H), 3.89–3.83 (m, 1H), 2.19–1.80 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H). (B) 7.44 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 2H), 7.39–7.27 (m, 3H), 5.17 (d, *J* = 4.4 Hz, 1H), 5.09 (s, 1H), 4.25–4.06 (m, 2H), 3.89–3.83 (m, 1H), 3.81–3.77 (m, 1H), 2.19–1.80 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 171.4, 137.2, 128.5, 128.4, 127.2, 102.7, 75.8, 67.5, 61.3, 32.6, 23.3, 14.2. (B) 171.4, 136.6, 128.64, 128.56, 127.4, 103.2, 77.4, 67.7, 61.1, 32.5, 23.6, 14.2 ppm.

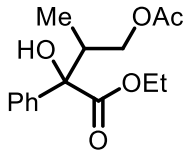
LRMS (ESI) Calcd. for $C_{14}H_{18}O_4$, $[M+Na]^+$: 273, Found: 273

FTIR (neat): 2981, 1747.


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ethyl 4-acetoxy-2-hydroxy-3-methyl-2-phenylbutanoate (3.8a).



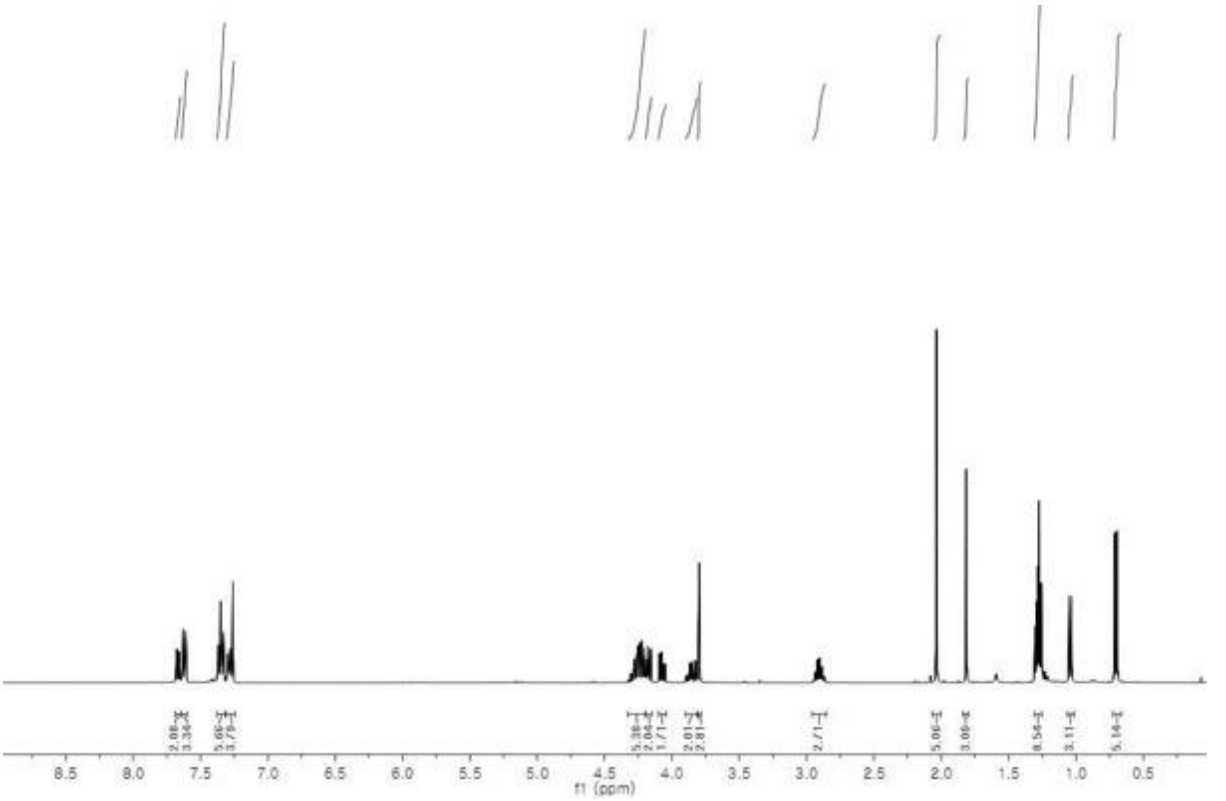
In accordance with Procedure B, **3.1a** (0.2 mmol, 100 mol%) was reacted with **3.2f** (13 x 100 mm pressure tube, 0.11 mL, 1.0 mmol, 500 mol%) in toluene (2.0 M) at 140 ^{o}C for a 40 hour period. Flash column chromatography (SiO_2: 5-7% ethyl acetate/hexanes) provided the title compound (33.6 mg, 0.12 mmol, *d.r.* = 1.6:1) as a pale yellow oil in 60% yield.

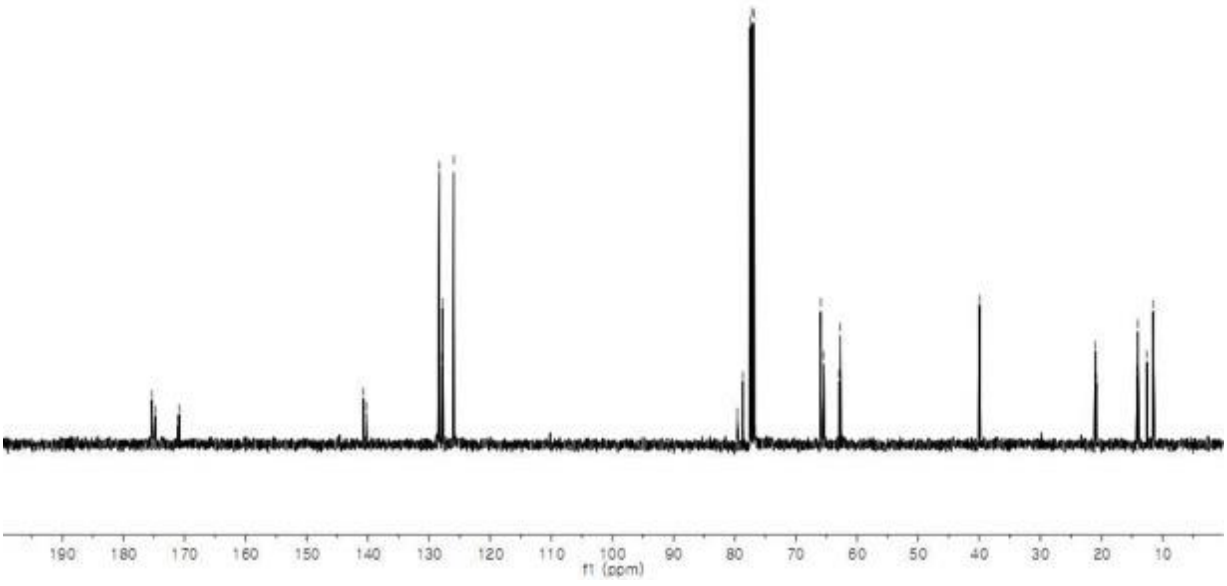
^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.62 (ddd, *J* = 3.4, 1.9, 1.9 Hz, 2H), 7.35 (ddd, *J* = 11.8, 4.6 Hz, 3H), 4.33–4.15 (m, 3H), 4.07 (dd, *J* = 11.0, 6.5 Hz, 1H), 3.80 (s, 1H), 2.96–2.86 (m, 1H), 2.04 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H). (minor) 7.66 (ddd, *J* = 3.4, 1.9, 1.9 Hz, 2H), 7.31–7.25 (m, 3H), 4.33–4.20 (m, 2H), 3.90–3.81 (m, 2H), 3.80 (s, 1H), 2.96–2.86 (m, 1H), 1.81 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.3, 170.8, 140.8, 128.3, 127.8, 126.0, 78.7, 66.0, 62.7, 40.0, 21.0, 14.1, 11.6. (minor) 174.7, 171.1, 140.2, 128.4, 127.9, 125.9, 79.6, 65.5, 62.9, 40.1, 20.8, 14.2, 12.6 ppm.

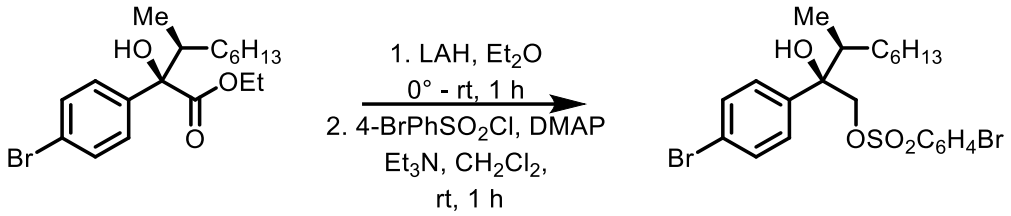
LRMS (ESI) Calcd. for $C_{15}H_{20}O_5$, $[M+Na]^+$: 303, Found: 303

FTIR (neat): 3494, 2981, 1727, 1231.


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

2-(4-bromophenyl)-2-hydroxy-3-methylnonyl 4-bromobenzenesulfonate (3.4b Derivative).



An ethereal solution (5 mL) of **3.4b** (1.39 g, 3.7 mmol) was added dropwise to a 100 mL round-bottom flask charged with an ethereal (30 mL, 0.12 M) suspension of LAH (709 mg, 18.7 mmol) at 0°C. The reaction was removed from the ice-bath and was allowed to stir for a 1 hour period. Distilled water (1 mL) was added slowly. Distilled water (3 ml) and 15% NaOH aqueous (1 mL) were added to the reaction mixture. To the vigorously stirred solution was added portions of $MgSO_4$ until the reaction mixture solidified. The reaction mixture was filtered through a fritted glass funnel with the aid of ether. The filtrate was evaporated under reduced pressure and was used in the next step without further purification. To the crude diol (1.16 g, 3.5 mmol) was added dichloromethane (30 ml, 1.1 M), 4-bromobenzenesulfonyl chloride (996 mg, 3.9 mmol), DMAP (42 mg, 0.35 mmol) and Et_3N (1 mL, 7.1 mmol). The reaction was allowed to stir at ambient temperature for a 1 hour period. $NaHCO_3$ (10 mL) and distilled water (10 ml) were added to the reaction mixture. The mixture was transferred to a separatory funnel and extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were washed with brine (1 x 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude 4b derivative residue was subjected to column chromatography (SiO_2: 20% ethyl acetate/hexanes) to give the title compound (1.7 g, 3.3 mmol) in 90% yield as a white solid.

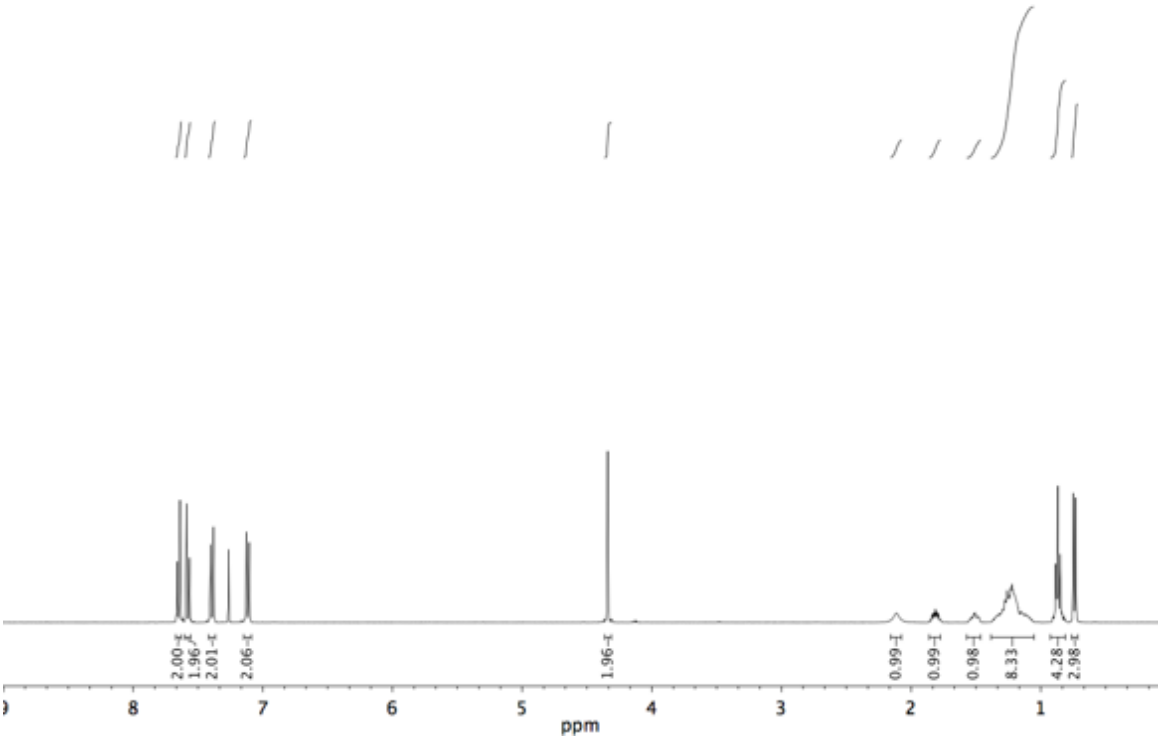
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.39. (d, *J* = 8.6, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 4.34 (s, 2H), 2.11 (s, 1H), 1.86–1.76 (m, 1H), 1.55–1.46 (m, 1H), 1.37–1.05 (m, 8H), 0.91–0.80 (m, 4H), 0.74 (d, *J* = 6.9 Hz, 2H) ppm.

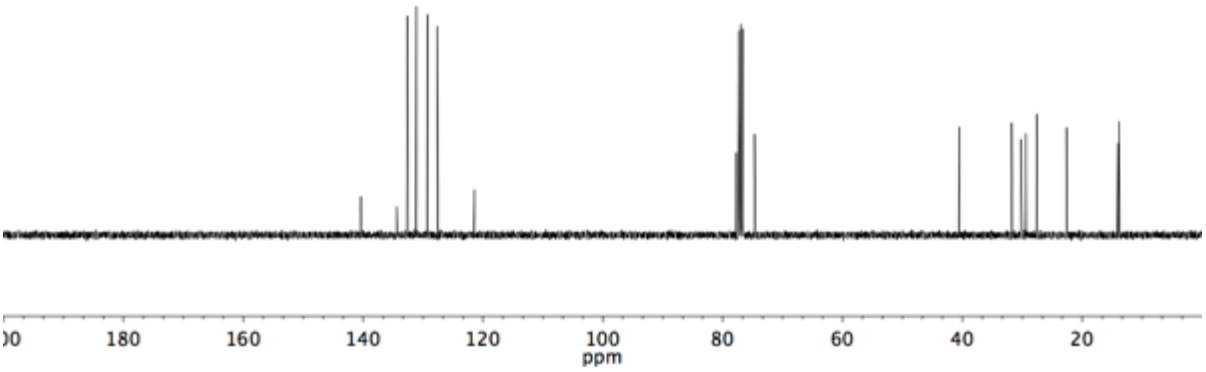
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 134.4, 132.6, 131.1, 129.2, 127.6, 74.7, 40.5, 31.8, 30.2, 29.4, 27.6, 22.6, 14.0, 13.8 ppm.

LRMS (ESI-MS) Calcd. for $C_{22}H_{28}Br_2O_4$ $[M+Na]^+$: 571, Found: 571

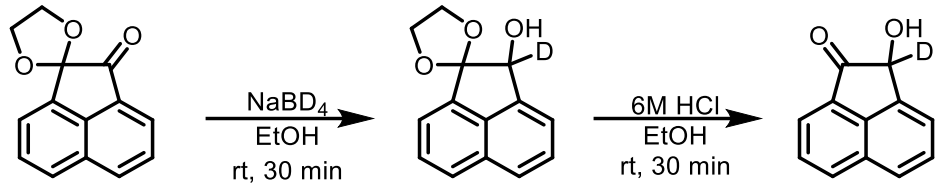
FTIR (neat): 3610, 2927, 1727, 1577

MP: 98–100 ºC.


2.00
1.96
2.01
2.06
1.96
0.99
0.99
0.98
8.33
4.28
2.98
8
7
6
5
4
3
2
1
ppm


180
160
140
120
100
80
60
40
20
ppm

2-hydroxyacenaphtylen-1(2H)-one-2-d (*deuterio*-3.1k).



To a flame-dried 50 mL round-bottom flask charged with 2*H*-spiro[acenaphthylene-1,2'-[1,3]dioxolan]-2-one (891 mg, 3.9 mmol) was added ethanol (20 ml, 0.2 M). $NaBD_4$ (180 mg, 4.3 mmol) was added portionwise. The reaction mixture was allowed to stir at ambient temperature for 30 min. Distilled water was added and the reaction mixture was allowed to stir until bubbling stopped. The mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine (1 x 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure. Without further purification the crude alcohol residue was added ethanol (20 mL) and 6.0 M HCl aqueous (15 ml). The reaction mixture was allowed to stir at ambient temperature for the stated time. Distilled water was added and the mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine (1 x 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude solid was subjected to column chromatography (SiO_2: 15% ethyl acetate in hexanes) to give the title compound (0.69 g, 3.7 mmol) in 95% yield as a white solid.

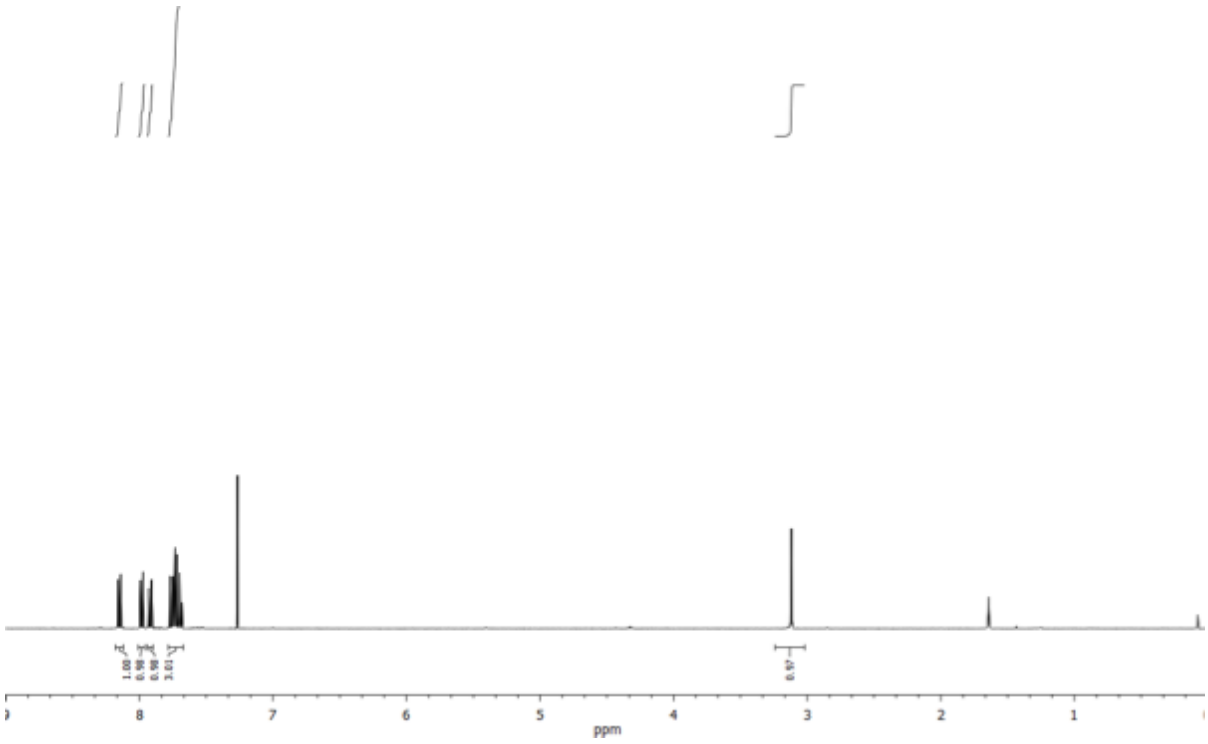
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.1 Hz, 1H), 7.92. (dd, *J* = 8.1, 1.1 Hz, 1H), 7.79–7.66 (m, 3H), 3.12 (s, 1H) ppm.

^{2}H NMR (77 MHz, $CHCl_3$): δ 5.37 (s, 1D) ppm.

HRMS (ESI-MS) Calcd. for $C_{12}H_7DO_2$ $[M+Na]^+$: 208.0479, Found: 208.0460

FTIR (neat): 3400, 3064, 1702

MP: 160–162 °C.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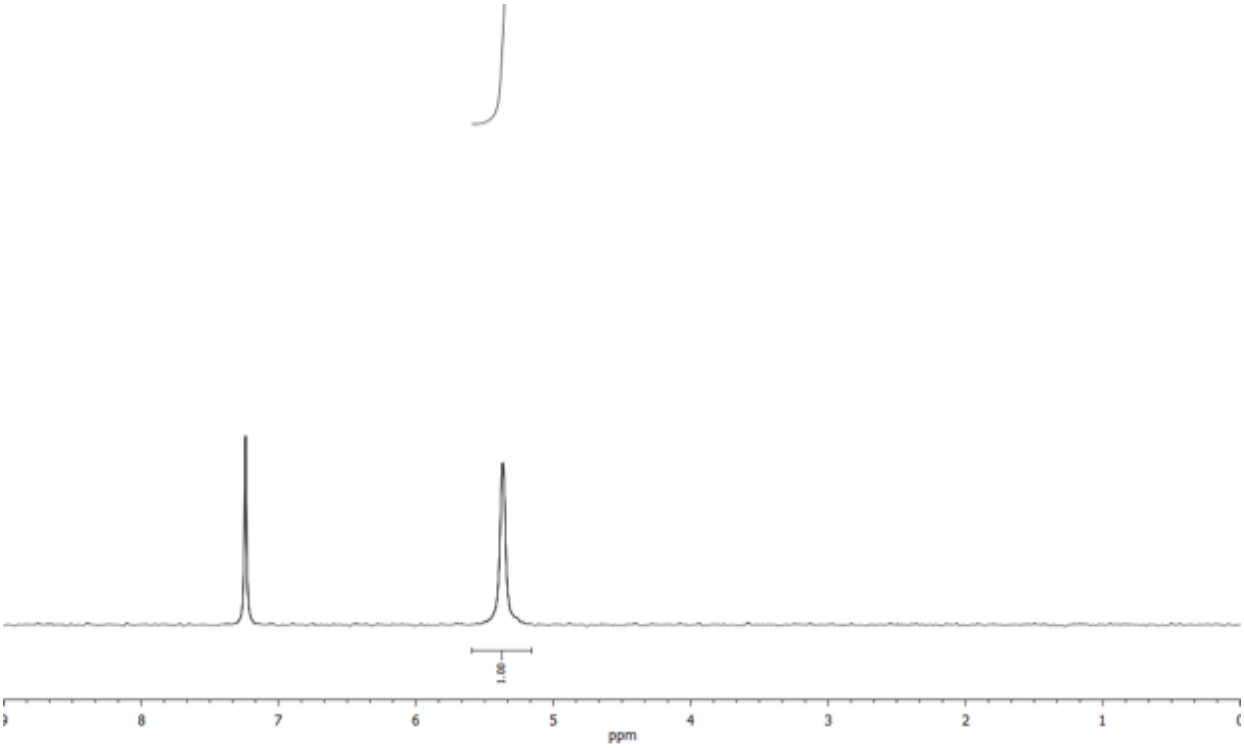
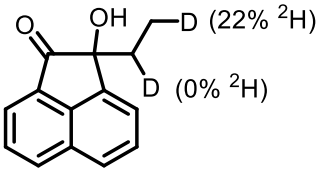
0.98
3.13
6.97
8
7
6
5
4
3
2
1
ppm


1.00
8
7
6
5
4
3
2
1
ppm

2-(ethyl-1,2-d2)-2-hydroxyacenaphthylen-1(2H)-one (*deuterio*-3.3k).



In accordance with Procedure A, *deuterio*-**3.1k** (0.2 mmol, 100 mol%) was reacted with ethylene (15 x 125 mm pressure tube, 0.82 mmol, 410 mol%) in toluene (2.0 M) at 130 °C for a 48 hour period. Flash column chromatography (SiO_2: 5-15% ethyl acetate/hexanes) provided the title compound (18.0 mg, 0.08 mmol) in 42% yield as a white solid.

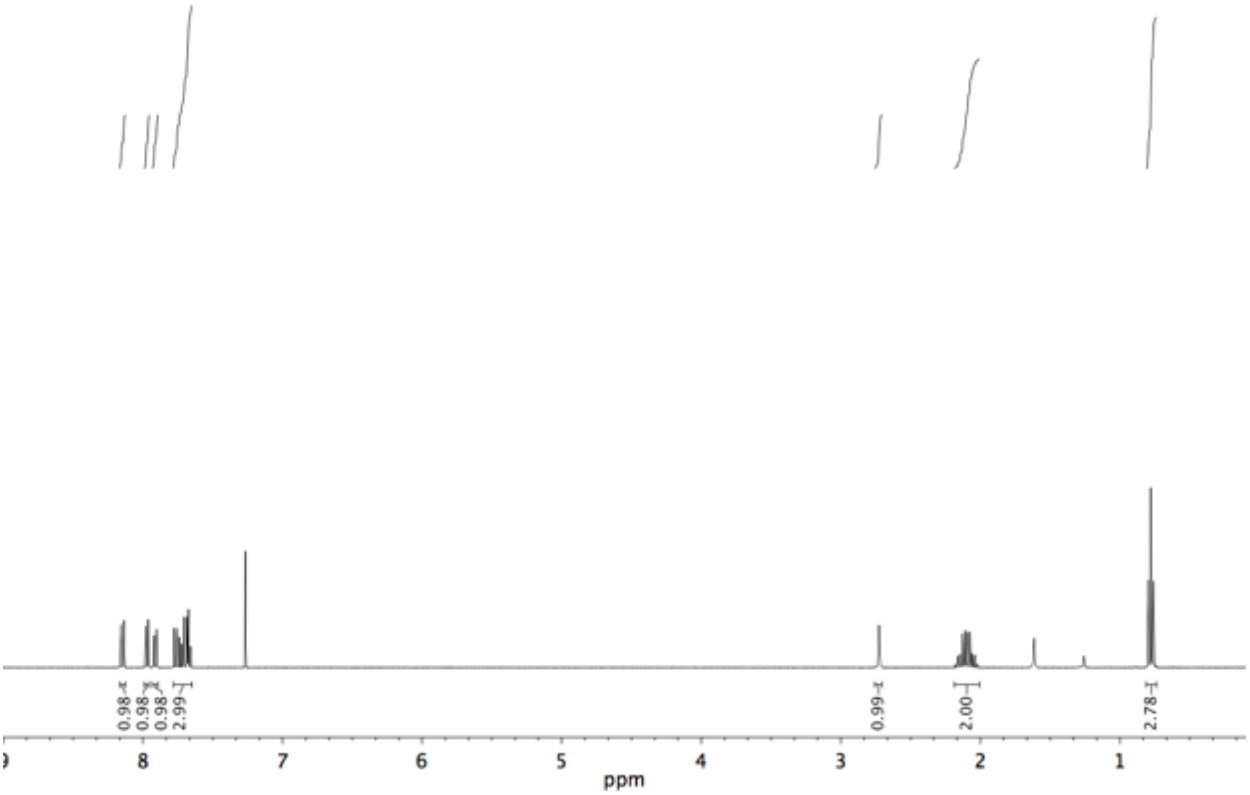
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.79–7.64 (m, 3H), 2.72 (s, 1H), 2.19–2.01 (m, 2H), 0.78 (t, *J* = 7.5 Hz, 2.78H) ppm.

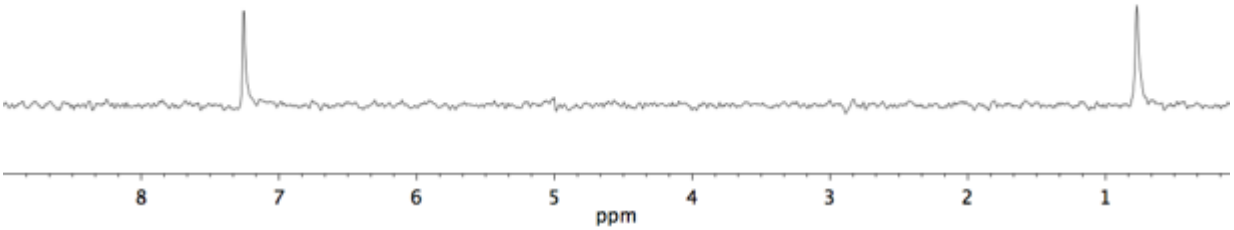
^{2}H NMR (77 MHz, $CHCl_3$): δ 0.77 (s, 0.22H) ppm.

HRMS (ESI-MS) Calcd. for $C_{14}H_{11}DO_2$ $[M+Na]^+$: 236.0792, Found: 236.0781

FTIR (neat): 3370, 2973, 2927, 1716

MP: 92–93 °C.


0.98
0.98
0.98
2.99
0.99
2.00
2.78
8
7
6
5
4
3
2
1
ppm


8
7
6
5
4
3
2
1
ppm

Crystallographic Data

X-ray Experimental for complex **$Os_3(CO)_{11}$(XPhos)**:

Crystals grew as yellow prisms by vapor diffusion of pentane and methanol. The data crystal had approximate dimensions; 0.28 x 0.12 x 0.07 mm. The data were collected on a diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 3355 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 2 seconds per frame with a detector offset of +/- 40.8° and 5 seconds per frame with a detector offset of +/- 106.8°. The data were collected at 100 K. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms . The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma (F_o))^2 + (0.0178*P)^2 + (11.8122*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0517, with R(F) equal to 0.0222 and a goodness of fit, S, = 1.00. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[25] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[26] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 3.6. Crystal data and structure refinement for **$Os_3(CO)_{11}$(XPhos)**.

Empirical formula	C44 H49 O11 Os3 P	
Formula weight	1355.40	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.6048(2) Å	α= 74.3970(10)°.
	b = 13.5575(2) Å	β= 75.4040(10)°.
	c = 15.1224(2) Å	γ= 84.1860(10)°.
Volume	2216.17(6) $Å^3$	
Z	2	
Density (calculated)	2.031 Mg/m^3	
Absorption coefficient	16.715 mm^{-1}	
F(000)	1288	
Crystal size	0.280 x 0.120 x 0.070 mm^3	
Theta range for data collection	3.121 to 73.521°.	
Index ranges	-14<=h<=14, -16<=k<=16, -18<=l<=18	
Reflections collected	40515	
Independent reflections	8704 [R(int) = 0.0304]	
Completeness to theta = 67.684°	99.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.183	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8704 / 0 / 538	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR2 = 0.0515	
R indices (all data)	R1 = 0.0229, wR2 = 0.0517	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.482 and -1.160 e.$Å^{-3}$	

Table 3.7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$Os_3(CO)_{11}$(XPhos)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	5953(3)	7616(3)	3080(3)	15(1)
C2	5537(3)	6831(3)	2794(3)	15(1)
C3	4554(3)	6289(3)	3407(3)	20(1)
C4	3934(3)	6536(3)	4232(3)	20(1)
C5	4275(3)	7368(3)	4464(3)	18(1)
C6	5277(3)	7885(3)	3901(3)	15(1)
C7	5925(3)	6554(3)	1859(3)	16(1)
C8	6807(3)	5774(3)	1715(3)	16(1)
C9	7010(3)	5467(3)	880(3)	18(1)
C10	6386(3)	5906(3)	181(3)	17(1)
C11	5513(3)	6656(3)	351(3)	18(1)
C12	5262(3)	6976(3)	1186(3)	16(1)
C13	7492(3)	5247(3)	2456(3)	18(1)
C14	6873(4)	4286(3)	3113(3)	29(1)
C15	8788(4)	4978(3)	2030(3)	26(1)
C16	6690(3)	5522(3)	-714(3)	22(1)
C17	7977(4)	5736(5)	-1247(4)	48(1)
C18	5861(4)	5947(3)	-1375(3)	26(1)
C19	4217(3)	7744(3)	1353(3)	21(1)
C20	4236(4)	8675(3)	519(3)	28(1)
C21	3029(4)	7216(4)	1605(4)	32(1)
C22	8089(3)	8103(3)	1441(2)	14(1)
C23	7445(3)	8699(3)	677(3)	17(1)
C24	7942(3)	8384(3)	-246(3)	21(1)
C25	9275(4)	8563(3)	-598(3)	25(1)
C26	9934(3)	8006(3)	161(3)	22(1)
C27	9434(3)	8298(3)	1096(3)	18(1)
C28	6899(3)	9653(3)	2540(3)	15(1)
C29	7921(3)	10397(3)	2082(3)	16(1)

C30	7517(3)	11474(3)	2221(3)	20(1)
C31	6418(3)	11870(3)	1842(3)	23(1)
C32	5414(3)	11115(3)	2263(3)	22(1)
C33	5808(3)	10040(3)	2125(3)	18(1)
C34	7386(3)	6604(3)	4465(3)	17(1)
C35	9584(3)	6633(3)	3280(3)	17(1)
C36	9815(3)	8612(3)	3067(3)	17(1)
C37	6432(3)	7798(3)	5795(3)	20(1)
C38	7772(3)	8993(3)	6413(3)	20(1)
C39	6619(3)	9890(3)	4887(3)	20(1)
C40	8967(3)	9707(3)	4439(3)	18(1)
C41	10802(3)	8158(3)	4680(3)	20(1)
C42	10581(3)	6074(3)	5172(3)	19(1)
C43	8269(3)	6242(3)	6117(3)	18(1)
C44	9858(3)	7355(3)	6569(3)	21(1)
O1	6715(2)	5983(2)	4806(2)	18(1)
O2	10250(2)	6033(2)	3013(2)	26(1)
O3	10578(2)	9119(2)	2610(2)	21(1)
O4	5651(2)	7287(2)	6150(2)	23(1)
O5	7788(3)	9100(2)	7133(2)	29(1)
O6	6024(2)	10600(2)	4712(2)	26(1)
O7	9631(2)	10315(2)	4000(2)	22(1)
O8	11584(2)	8660(2)	4289(2)	24(1)
O9	11209(2)	5396(2)	5031(2)	27(1)
O10	7581(2)	5654(2)	6529(2)	22(1)
O11	10077(3)	7445(2)	7241(2)	28(1)
Os1	8583(1)	7636(1)	3775(1)	12(1)
Os2	7710(1)	8783(1)	5217(1)	14(1)
Os3	9551(1)	7198(1)	5429(1)	14(1)
P1	7390(1)	8278(1)	2639(1)	12(1)

Table 3.8. Bond lengths [Å] and angles [°] of **$Os_3(CO)_{11}$(XPhos)**.

C1-C6	1.408(5)		
C1-C2	1.419(5)	C17-H17A	0.98
C1-P1	1.858(3)	C17-H17B	0.98
C2-C3	1.403(5)	C17-H17C	0.98
C2-C7	1.507(5)	C18-H18A	0.98
C3-C4	1.382(5)	C18-H18B	0.98
C3-H3	0.95	C18-H18C	0.98
C4-C5	1.387(5)	C19-C20	1.523(6)
C4-H4	0.95	C19-C21	1.532(5)
C5-C6	1.383(5)	C19-H19	1.00
C5-H5	0.95	C20-H20A	0.98
C6-H6	0.95	C20-H20B	0.98
C7-C12	1.396(5)	C20-H20C	0.98
C7-C8	1.417(5)	C21-H21A	0.98
C8-C9	1.391(5)	C21-H21B	0.98
C8-C13	1.516(5)	C21-H21C	0.98
C9-C10	1.400(6)	C22-C23	1.536(5)
C9-H9	0.95	C22-C27	1.541(5)
C10-C11	1.388(5)	C22-P1	1.856(4)
C10-C16	1.525(5)	C22-H22	1.00
C11-C12	1.397(5)	C23-C24	1.527(5)
C11-H11	0.95	C23-H23A	0.99
C12-C19	1.534(5)	C23-H23B	0.99
C13-C14	1.528(5)	C24-C25	1.525(5)
C13-C15	1.529(5)	C24-H24A	0.99
C13-H13	1.00	C24-H24B	0.99
C14-H14A	0.98	C25-C26	1.528(6)
C14-H14B	0.98	C25-H25A	0.99
C14-H14C	0.98	C25-H25B	0.99
C15-H15A	0.98	C26-C27	1.528(5)
C15-H15B	0.98	C26-H26A	0.99
C15-H15C	0.98	C26-H26B	0.99
C16-C17	1.522(6)	C27-H27A	0.99
C16-C18	1.524(6)	C27-H27B	0.99
C16-H16	1.00	C28-C29	1.535(5)

C28-C33	1.536(5)	C36-Os1	1.947(4)
C28-P1	1.870(4)	C37-O4	1.127(5)
C28-H28	1.00	C37-Os2	1.968(4)
C29-C30	1.541(5)	C38-O5	1.141(5)
C29-H29A	0.99	C38-Os2	1.924(4)
C29-H29B	0.99	C39-O6	1.138(5)
C30-C31	1.519(5)	C39-Os2	1.906(4)
C30-H30A	0.99	C40-O7	1.136(5)
C30-H30B	0.99	C40-Os2	1.947(4)
C31-C32	1.526(5)	C41-O8	1.128(5)
C31-H31A	0.99	C41-Os3	1.961(4)
C31-H31B	0.99	C42-O9	1.146(5)
C32-C33	1.536(5)	C42-Os3	1.902(4)
C32-H32A	0.99	C43-O10	1.128(5)
C32-H32B	0.99	C43-Os3	1.965(4)
C33-H33A	0.99	C44-O11	1.147(5)
C33-H33B	0.99	C44-Os3	1.915(4)
C34-O1	1.130(5)	Os1-P1	2.4028(9)
C34-Os1	1.963(4)	Os1-Os3	2.8912(2)
C35-O2	1.147(5)	Os1-Os2	2.9312(2)
C35-Os1	1.884(4)	Os2-Os3	2.8857(2)
C36-O3	1.137(5)		

C6-C1-C2	118.1(3)	C6-C5-H5	120.4
C6-C1-P1	110.9(3)	C4-C5-H5	120.4
C2-C1-P1	130.5(3)	C5-C6-C1	122.5(3)
C3-C2-C1	117.6(3)	C5-C6-H6	118.8
C3-C2-C7	113.5(3)	C1-C6-H6	118.8
C1-C2-C7	128.6(3)	C12-C7-C8	120.2(3)
C4-C3-C2	123.0(3)	C12-C7-C2	117.7(3)
C4-C3-H3	118.5	C8-C7-C2	121.4(3)
C2-C3-H3	118.5	C9-C8-C7	118.2(4)
C3-C4-C5	119.1(3)	C9-C8-C13	119.8(3)
C3-C4-H4	120.4	C7-C8-C13	121.9(3)
C5-C4-H4	120.4	C8-C9-C10	122.5(3)
C6-C5-C4	119.2(3)	C8-C9-H9	118.7

C10-C9-H9	118.7	H17A-C17-H17B	109.5
C11-C10-C9	117.8(3)	C16-C17-H17C	109.5
C11-C10-C16	124.0(4)	H17A-C17-H17C	109.5
C9-C10-C16	118.2(3)	H17B-C17-H17C	109.5
C10-C11-C12	121.7(4)	C16-C18-H18A	109.5
C10-C11-H11	119.1	C16-C18-H18B	109.5
C12-C11-H11	119.1	H18A-C18-H18B	109.5
C7-C12-C11	119.5(3)	C16-C18-H18C	109.5
C7-C12-C19	122.0(3)	H18A-C18-H18C	109.5
C11-C12-C19	118.4(3)	H18B-C18-H18C	109.5
C8-C13-C14	111.1(3)	C20-C19-C21	109.6(3)
C8-C13-C15	113.0(3)	C20-C19-C12	113.6(3)
C14-C13-C15	109.9(3)	C21-C19-C12	110.4(3)
C8-C13-H13	107.5	C20-C19-H19	107.7
C14-C13-H13	107.5	C21-C19-H19	107.7
C15-C13-H13	107.5	C12-C19-H19	107.7
C13-C14-H14A	109.5	C19-C20-H20A	109.5
C13-C14-H14B	109.5	C19-C20-H20B	109.5
H14A-C14-H14B	109.5	H20A-C20-H20B	109.5
C13-C14-H14C	109.5	C19-C20-H20C	109.5
H14A-C14-H14C	109.5	H20A-C20-H20C	109.5
H14B-C14-H14C	109.5	H20B-C20-H20C	109.5
C13-C15-H15A	109.5	C19-C21-H21A	109.5
C13-C15-H15B	109.5	C19-C21-H21B	109.5
H15A-C15-H15B	109.5	H21A-C21-H21B	109.5
C13-C15-H15C	109.5	C19-C21-H21C	109.5
H15A-C15-H15C	109.5	H21A-C21-H21C	109.5
H15B-C15-H15C	109.5	H21B-C21-H21C	109.5
C17-C16-C10	110.8(3)	C23-C22-C27	109.6(3)
C17-C16-C18	109.9(4)	C23-C22-P1	114.1(2)
C10-C16-C18	114.2(3)	C27-C22-P1	115.2(2)
C17-C16-H16	107.2	C23-C22-H22	105.7
C10-C16-H16	107.2	C27-C22-H22	105.7
C18-C16-H16	107.2	P1-C22-H22	105.7
C16-C17-H17A	109.5	C24-C23-C22	111.0(3)
C16-C17-H17B	109.5	C24-C23-H23A	109.4

C22-C23-H23A	109.4	C30-C29-H29A	109.5
C24-C23-H23B	109.4	C28-C29-H29B	109.5
C22-C23-H23B	109.4	C30-C29-H29B	109.5
H23A-C23-H23B	108.0	H29A-C29-H29B	108.1
C25-C24-C23	110.8(3)	C31-C30-C29	111.3(3)
C25-C24-H24A	109.5	C31-C30-H30A	109.4
C23-C24-H24A	109.5	C29-C30-H30A	109.4
C25-C24-H24B	109.5	C31-C30-H30B	109.4
C23-C24-H24B	109.5	C29-C30-H30B	109.4
H24A-C24-H24B	108.1	H30A-C30-H30B	108.0
C24-C25-C26	110.5(3)	C30-C31-C32	111.7(3)
C24-C25-H25A	109.5	C30-C31-H31A	109.3
C26-C25-H25A	109.5	C32-C31-H31A	109.3
C24-C25-H25B	109.5	C30-C31-H31B	109.3
C26-C25-H25B	109.5	C32-C31-H31B	109.3
H25A-C25-H25B	108.1	H31A-C31-H31B	107.9
C25-C26-C27	112.5(3)	C31-C32-C33	112.4(3)
C25-C26-H26A	109.1	C31-C32-H32A	109.1
C27-C26-H26A	109.1	C33-C32-H32A	109.1
C25-C26-H26B	109.1	C31-C32-H32B	109.1
C27-C26-H26B	109.1	C33-C32-H32B	109.1
H26A-C26-H26B	107.8	H32A-C32-H32B	107.9
C26-C27-C22	110.3(3)	C32-C33-C28	109.6(3)
C26-C27-H27A	109.6	C32-C33-H33A	109.7
C22-C27-H27A	109.6	C28-C33-H33A	109.7
C26-C27-H27B	109.6	C32-C33-H33B	109.7
C22-C27-H27B	109.6	C28-C33-H33B	109.7
H27A-C27-H27B	108.1	H33A-C33-H33B	108.2
C29-C28-C33	110.8(3)	O1-C34-Os1	175.0(3)
C29-C28-P1	113.4(2)	O2-C35-Os1	175.1(3)
C33-C28-P1	117.5(2)	O3-C36-Os1	173.9(3)
C29-C28-H28	104.5	O4-C37-Os2	175.1(3)
C33-C28-H28	104.5	O5-C38-Os2	178.4(3)
P1-C28-H28	104.5	O6-C39-Os2	174.2(3)
C28-C29-C30	110.5(3)	O7-C40-Os2	173.9(3)
C28-C29-H29A	109.5	O8-C41-Os3	174.3(3)

O9-C42-Os3	178.8(4)	C37-Os2-Os3	92.57(11)
O10-C43-Os3	176.1(3)	C39-Os2-Os1	114.06(11)
O11-C44-Os3	178.0(4)	C38-Os2-Os1	148.27(12)
C35-Os1-C36	87.45(15)	C40-Os2-Os1	83.49(10)
C35-Os1-C34	89.96(15)	C37-Os2-Os1	87.80(11)
C36-Os1-C34	177.40(15)	Os3-Os2-Os1	59.602(5)
C35-Os1-P1	102.81(11)	C42-Os3-C44	103.39(17)
C36-Os1-P1	91.93(11)	C42-Os3-C41	90.45(15)
C34-Os1-P1	88.65(11)	C44-Os3-C41	90.20(16)
C35-Os1-Os3	92.71(11)	C42-Os3-C43	89.45(16)
C36-Os1-Os3	91.32(11)	C44-Os3-C43	92.86(16)
C34-Os1-Os3	88.79(11)	C41-Os3-C43	176.88(15)
P1-Os1-Os3	164.27(2)	C42-Os3-Os2	158.11(12)
C35-Os1-Os2	152.12(11)	C44-Os3-Os2	98.38(12)
C36-Os1-Os2	92.48(10)	C41-Os3-Os2	91.84(11)
C34-Os1-Os2	89.81(10)	C43-Os3-Os2	87.10(11)
P1-Os1-Os2	105.05(2)	C42-Os3-Os1	97.40(12)
Os3-Os1-Os2	59.417(5)	C44-Os3-Os1	159.09(12)
C39-Os2-C38	97.60(16)	C41-Os3-Os1	87.35(11)
C39-Os2-C40	86.50(16)	C43-Os3-Os1	89.57(11)
C38-Os2-C40	96.96(16)	Os2-Os3-Os1	60.982(5)
C39-Os2-C37	92.67(16)	C22-P1-C1	108.44(16)
C38-Os2-C37	93.00(16)	C22-P1-C28	109.09(16)
C40-Os2-C37	170.03(15)	C1-P1-C28	102.42(16)
C39-Os2-Os3	171.59(11)	C22-P1-Os1	114.51(12)
C38-Os2-Os3	88.69(12)	C1-P1-Os1	108.54(12)
C40-Os2-Os3	87.20(11)	C28-P1-Os1	113.05(12)

Table 3.9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **$Os_3(CO)_{11}$(XPhos)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	15(2)	13(2)	15(2)	-2(1)	-1(1)	-4(1)
C2	15(2)	14(2)	15(2)	-2(1)	-3(1)	-1(1)
C3	20(2)	18(2)	20(2)	-3(2)	-1(2)	-8(1)
C4	15(2)	18(2)	23(2)	-1(2)	0(1)	-8(1)
C5	15(2)	20(2)	16(2)	-4(2)	0(1)	-2(1)
C6	12(2)	16(2)	16(2)	-2(1)	-3(1)	-2(1)
C7	15(2)	12(2)	19(2)	-4(1)	0(1)	-6(1)
C8	16(2)	16(2)	16(2)	-3(1)	-2(1)	-6(1)
C9	17(2)	16(2)	22(2)	-6(2)	-2(1)	-1(1)
C10	18(2)	22(2)	13(2)	-5(2)	-1(1)	-8(1)
C11	20(2)	19(2)	16(2)	-1(2)	-5(1)	-6(1)
C12	15(2)	15(2)	17(2)	-3(2)	-1(1)	-5(1)
C13	20(2)	19(2)	16(2)	-7(2)	-5(1)	-3(1)
C14	34(2)	26(2)	25(2)	1(2)	-8(2)	-8(2)
C15	23(2)	27(2)	28(2)	-7(2)	-7(2)	3(2)
C16	23(2)	27(2)	18(2)	-9(2)	-4(2)	0(2)
C17	26(2)	91(5)	29(3)	-28(3)	0(2)	1(3)
C18	26(2)	35(2)	20(2)	-11(2)	-3(2)	-4(2)
C19	21(2)	21(2)	23(2)	-8(2)	-8(2)	2(2)
C20	30(2)	24(2)	34(2)	-6(2)	-14(2)	2(2)
C21	19(2)	33(2)	41(3)	-7(2)	-3(2)	0(2)
C22	15(2)	14(2)	12(2)	-2(1)	0(1)	-5(1)
C23	20(2)	16(2)	15(2)	-1(1)	-3(1)	-5(1)
C24	24(2)	25(2)	14(2)	-5(2)	0(2)	-9(2)
C25	28(2)	30(2)	12(2)	-4(2)	3(2)	-10(2)
C26	18(2)	26(2)	20(2)	-7(2)	4(2)	-6(2)
C27	15(2)	22(2)	15(2)	-3(2)	1(1)	-6(1)
C28	15(2)	14(2)	14(2)	-3(1)	-2(1)	-2(1)
C29	16(2)	12(2)	19(2)	0(1)	-3(1)	-5(1)
C30	23(2)	16(2)	21(2)	-4(2)	-3(2)	-7(1)

C31	25(2)	15(2)	29(2)	-6(2)	-7(2)	-1(2)
C32	19(2)	18(2)	28(2)	-7(2)	-4(2)	0(1)
C33	16(2)	17(2)	20(2)	-3(2)	-4(1)	-2(1)
C34	19(2)	16(2)	15(2)	-3(2)	-5(1)	3(1)
C35	17(2)	20(2)	14(2)	-3(2)	-5(1)	-4(1)
C36	21(2)	18(2)	16(2)	-6(2)	-9(2)	4(2)
C37	24(2)	20(2)	17(2)	-7(2)	-6(2)	1(2)
C38	18(2)	22(2)	22(2)	-7(2)	-4(2)	-3(1)
C39	19(2)	26(2)	14(2)	-6(2)	1(1)	-5(2)
C40	20(2)	18(2)	20(2)	-9(2)	-7(2)	0(2)
C41	26(2)	14(2)	21(2)	-6(2)	-10(2)	4(2)
C42	16(2)	17(2)	27(2)	-7(2)	-6(2)	-4(1)
C43	23(2)	20(2)	12(2)	-3(2)	-8(2)	2(2)
C44	24(2)	16(2)	22(2)	-4(2)	-4(2)	-4(1)
O1	17(1)	17(1)	18(1)	1(1)	-2(1)	-6(1)
O2	22(1)	23(1)	31(2)	-12(1)	-1(1)	3(1)
O3	18(1)	22(1)	20(1)	-2(1)	0(1)	-11(1)
O4	22(1)	23(1)	24(2)	-7(1)	1(1)	-9(1)
O5	32(2)	38(2)	18(2)	-10(1)	-5(1)	-9(1)
O6	25(1)	23(2)	29(2)	-8(1)	-6(1)	4(1)
O7	23(1)	20(1)	24(2)	-6(1)	-4(1)	-7(1)
O8	20(1)	21(1)	29(2)	-3(1)	-4(1)	-6(1)
O9	19(1)	19(1)	45(2)	-10(1)	-5(1)	-1(1)
O10	24(1)	24(1)	16(1)	-1(1)	-2(1)	-9(1)
O11	41(2)	27(2)	22(2)	-4(1)	-15(1)	-6(1)
Os1	12(1)	13(1)	11(1)	-3(1)	-2(1)	-3(1)
Os2	14(1)	15(1)	14(1)	-5(1)	-2(1)	-3(1)
Os3	15(1)	14(1)	15(1)	-3(1)	-5(1)	-2(1)
P1	11(1)	13(1)	12(1)	-3(1)	-1(1)	-4(1)

Table 3.10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **$Os_3(CO)_{11}$(XPhos)**.

	x	y	z	U(eq)
H3	4303	5727	3248	24
H4	3283	6142	4635	24
H5	3825	7580	5004	21
H6	5518	8441	4074	18
H9	7595	4940	781	22
H11	5074	6959	-113	22
H13	7498	5733	2848	21
H14A	6070	4475	3435	43
H14B	7333	3959	3583	43
H14C	6817	3807	2743	43
H15A	8813	4454	1686	39
H15B	9210	4713	2536	39
H15C	9172	5593	1594	39
H16	6618	4761	-512	27
H17A	8080	6478	-1459	71
H17B	8169	5445	-1796	71
H17C	8509	5424	-829	71
H18A	5033	5825	-1023	40
H18B	6049	5604	-1891	40
H18C	5967	6685	-1637	40
H19	4266	7995	1907	25
H20A	5012	8992	338	43
H20B	3606	9172	698	43
H20C	4104	8460	-16	43
H21A	2959	6958	1075	49
H21B	2370	7709	1735	49
H21C	2997	6643	2167	49
H22	8013	7362	1487	17
H23A	6583	8566	898	21
H23B	7541	9443	567	21

H24A	7801	7649	-146	25
H24B	7523	8786	-730	25
H25A	9411	9306	-766	30
H25B	9590	8311	-1173	30
H26A	10787	8171	-66	27
H26B	9879	7257	268	27
H27A	9567	9031	1011	22
H27B	9854	7888	1576	22
H28	6641	9709	3208	18
H29A	8182	10433	1399	20
H29B	8607	10142	2369	20
H30A	7339	11450	2902	24
H30B	8172	11952	1890	24
H31A	6629	11989	1146	27
H31B	6140	12533	1993	27
H32A	4740	11376	1962	27
H32B	5129	11071	2947	27
H33A	6011	10064	1443	21
H33B	5149	9565	2444	21

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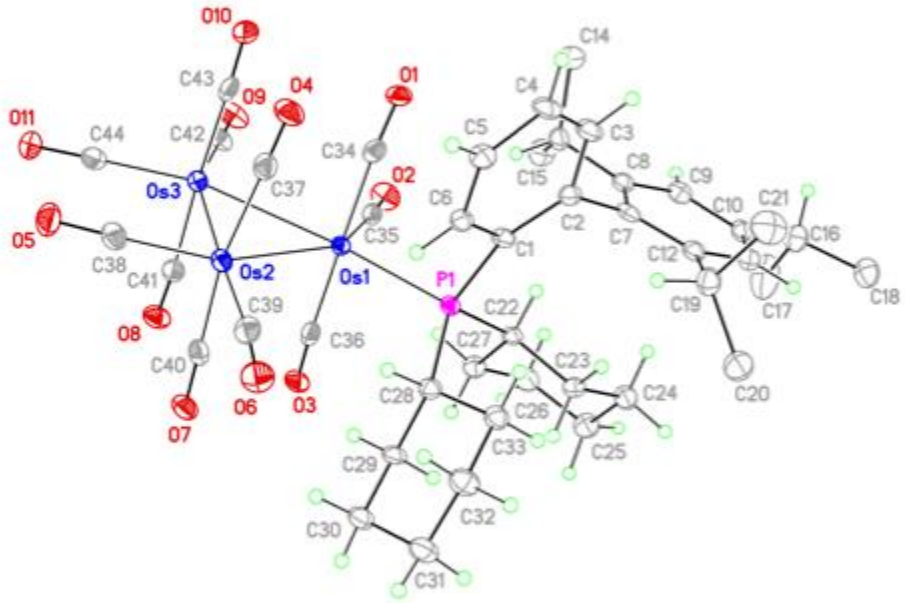
Table 3.11. Torsion angles [°] for **$Os_3(CO)_{11}$(XPhos)**.

C6-C1-C2-C3	-7.3(5)	C7-C8-C13-C15	-144.3(3)
P1-C1-C2-C3	163.6(3)	C11-C10-C16-C17	118.4(4)
C6-C1-C2-C7	165.6(4)	C9-C10-C16-C17	-62.6(5)
P1-C1-C2-C7	-23.5(6)	C11-C10-C16-C18	-6.4(5)
C1-C2-C3-C4	4.7(6)	C9-C10-C16-C18	172.7(3)
C7-C2-C3-C4	-169.2(4)	C7-C12-C19-C20	133.6(4)
C2-C3-C4-C5	1.3(6)	C11-C12-C19-C20	-49.5(5)
C3-C4-C5-C6	-4.6(6)	C7-C12-C19-C21	-102.9(4)
C4-C5-C6-C1	1.8(6)	C11-C12-C19-C21	74.0(4)
C2-C1-C6-C5	4.3(6)	C27-C22-C23-C24	58.4(4)
P1-C1-C6-C5	-168.3(3)	P1-C22-C23-C24	-170.7(2)
C3-C2-C7-C12	78.2(4)	C22-C23-C24-C25	-58.2(4)
C1-C2-C7-C12	-94.9(5)	C23-C24-C25-C26	55.4(4)
C3-C2-C7-C8	-91.9(4)	C24-C25-C26-C27	-55.0(4)
C1-C2-C7-C8	94.9(5)	C25-C26-C27-C22	55.8(4)
C12-C7-C8-C9	1.8(5)	C23-C22-C27-C26	-56.5(4)
C2-C7-C8-C9	171.7(3)	P1-C22-C27-C26	173.2(3)
C12-C7-C8-C13	-176.0(3)	C33-C28-C29-C30	57.9(4)
C2-C7-C8-C13	-6.0(5)	P1-C28-C29-C30	-167.4(3)
C7-C8-C9-C10	0.6(5)	C28-C29-C30-C31	-55.8(4)
C13-C8-C9-C10	178.4(3)	C29-C30-C31-C32	53.9(4)
C8-C9-C10-C11	-1.7(5)	C30-C31-C32-C33	-54.5(5)
C8-C9-C10-C16	179.2(3)	C31-C32-C33-C28	55.7(4)
C9-C10-C11-C12	0.5(5)	C29-C28-C33-C32	-57.3(4)
C16-C10-C11-C12	179.5(3)	P1-C28-C33-C32	170.0(3)
C8-C7-C12-C11	-3.0(5)	C23-C22-P1-C1	70.3(3)
C2-C7-C12-C11	-173.3(3)	C27-C22-P1-C1	-161.7(3)
C8-C7-C12-C19	173.9(3)	C23-C22-P1-C28	-40.6(3)
C2-C7-C12-C19	3.6(5)	C27-C22-P1-C28	87.5(3)
C10-C11-C12-C7	1.8(5)	C23-C22-P1-Os1	-168.4(2)
C10-C11-C12-C19	-175.2(3)	C27-C22-P1-Os1	-40.3(3)
C9-C8-C13-C14	-86.2(4)	C6-C1-P1-C22	-168.7(3)
C7-C8-C13-C14	91.6(4)	C2-C1-P1-C22	19.9(4)
C9-C8-C13-C15	37.9(5)	C6-C1-P1-C28	-53.5(3)

C2-C1-P1-C28	135.2(4)	C29-C28-P1-C1	-173.8(3)
C6-C1-P1-Os1	66.3(3)	C33-C28-P1-C1	-42.3(3)
C2-C1-P1-Os1	-105.0(4)	C29-C28-P1-Os1	69.6(3)
C29-C28-P1-C22	-59.0(3)	C33-C28-P1-Os1	-158.9(2)
C33-C28-P1-C22	72.4(3)		

Figure 3.3. View of **$Os_3(CO)_{11}$(XPhos)** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The methyl group hydrogen atoms were omitted for clarity.



X-ray Experimental for complex **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**:

Crystals grew as colorless laths by vapor diffusion using pentane and methanol. The data crystal had approximate dimensions; 0.43 x 0.08 x 0.02 mm. The data were collected using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 2084 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 10 seconds per frame with a detector offset of +/- 40.6° and 30 seconds per frame with a detector offset of +/- 106.8°. The data were collected at 100 K. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed.The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

One of the Os dimer complexes was disordered near a crystallographic mirror plane of symmetry at ½, y, z. The complex was displaced from the mirror by approximately 0.3Å. The disordered complex was refined using a large number of geometric and displacement parameter restraints. The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma (F_O))^2 + (0.1205*P)^2 + (64.9258*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.216, with R(F) equal to 0.0720 and a goodness of fit, S, = 1.07. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[1] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[2] Tables of

positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 3.12. Crystal data and structure refinement for **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**.

Empirical formula	C92 H128 O8 Os2 P2	
Formula weight	1804.28	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	P m c 21	
Unit cell dimensions	a = 36.3787(8) Å	α= 90°.
	b = 13.1217(6) Å	β= 90°.
	c = 17.3763(5) Å	γ = 90°.
Volume	8294.6(5) $Å^3$	
Z	4	
Density (calculated)	1.445 Mg/m^3	
Absorption coefficient	6.488 mm^{-1}	
F(000)	3704	
Crystal size	0.430 x 0.082 x 0.019 mm^3	
Theta range for data collection	2.429 to 73.404°.	
Index ranges	-45<=h<=40, -16<=k<=9, -21<=l<=21	
Reflections collected	48508	
Independent reflections	15805 [R(int) = 0.0500]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.364	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15805 / 3785 / 1440	
Goodness-of-fit on F^2	1.142	
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1993	
R indices (all data)	R1 = 0.0850, wR2 = 0.2157	
Absolute structure parameter	0.50(3)	
Extinction coefficient	0.00012(3)	
Largest diff. peak and hole	3.677 and -4.246 $e.Å^{-3}$	

Table 3.13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Os1	382(1)	6452(1)	4353(2)	13(1)
P1	1038(1)	6262(3)	4130(3)	21(1)
O1	310(3)	7198(8)	3269(6)	23(2)
O2	310(3)	5086(7)	3670(6)	20(2)
O3	393(3)	8512(6)	5106(8)	23(2)
O4	440(3)	5249(8)	5833(6)	29(2)
C1	1192(4)	6765(11)	3177(9)	20(2)
C2	1007(4)	6280(11)	2591(9)	21(3)
C3	1095(5)	6406(11)	1808(10)	27(3)
C4	1375(5)	7075(14)	1622(12)	36(3)
C5	1546(6)	7641(14)	2217(11)	31(3)
C6	1461(4)	7515(11)	2980(10)	25(3)
C7	1664(5)	8237(13)	3519(10)	33(3)
C8	2023(5)	8046(13)	3728(10)	35(3)
C9	2212(6)	8806(16)	4169(12)	47(4)
C10	2049(5)	9706(13)	4351(17)	49(3)
C11	1690(6)	9894(15)	4128(12)	45(4)
C12	1492(5)	9170(13)	3696(11)	35(3)
C13	2220(5)	7090(16)	3495(14)	46(4)
C14	2520(6)	7350(19)	2886(17)	61(6)
C15	2398(6)	6550(15)	4193(15)	53(5)
C16	2249(8)	10560(20)	4805(19)	80(6)
C17	2634(9)	10680(30)	4730(30)	107(10)
C18	2062(7)	10810(17)	5574(15)	58(5)
C19	1113(5)	9418(12)	3417(11)	34(3)
C20	1155(6)	10003(15)	2629(12)	44(4)
C21	881(5)	10059(13)	3985(13)	40(4)
C22	1175(4)	4906(10)	3958(9)	24(3)
C23	1594(5)	4808(12)	3816(12)	31(3)
C24	1700(6)	3695(13)	3578(13)	39(4)

C25	1554(5)	2930(12)	4175(12)	38(4)
C26	1149(5)	3031(9)	4283(17)	34(3)
C27	1032(5)	4108(10)	4525(9)	24(3)
C28	1349(4)	6719(12)	4888(9)	24(3)
C29	1220(5)	7742(11)	5220(10)	27(3)
C30	1492(6)	8220(13)	5788(12)	36(4)
C31	1541(7)	7469(16)	6463(13)	35(4)
C32	1666(5)	6440(11)	6193(12)	30(3)
C33	1400(5)	6005(13)	5583(11)	33(3)
C34	0	7387(12)	2968(10)	14(3)
C35	0	7804(15)	2141(11)	18(3)
C36	347(4)	8466(10)	2008(9)	23(3)
C37	345(4)	8841(13)	1182(10)	25(3)
C38	341(5)	7931(14)	639(10)	33(3)
C39	0	7259(15)	766(12)	24(4)
C40	0	6885(14)	1606(11)	21(4)
C41	0	9488(16)	1025(14)	31(4)
C42	0	4730(14)	3495(10)	15(3)
C43	0	3724(14)	3056(11)	14(3)
C44	-351(4)	3657(11)	2551(10)	24(3)
C45	-349(4)	2598(13)	2122(10)	29(3)
C46	-347(5)	1785(15)	2743(12)	35(4)
C47	0	1847(19)	3241(15)	36(4)
C48	0	2897(18)	3665(14)	36(4)
C49	0	2540(20)	1648(17)	39(5)
C50	395(4)	7703(9)	4846(9)	20(3)
C51	421(4)	5739(10)	5278(7)	19(2)
Os1A	4623(2)	8420(5)	6235(4)	62(1)
P1A	3966(3)	8458(7)	6463(7)	40(2)
O1A	4713(5)	7700(20)	7276(13)	53(5)
O2A	5331(5)	8010(30)	7338(13)	55(5)
O3A	4613(8)	6390(18)	5480(20)	53(7)
C45A	4625(6)	7190(20)	5800(20)	52(5)
O4A	4548(9)	9590(30)	4760(16)	55(8)
C46A	4572(6)	9090(30)	5297(16)	58(5)
C34A	5029(4)	7647(15)	7624(14)	57(4)

C35A	5041(6)	7120(20)	8435(13)	59(4)
C36A	5328(11)	6480(30)	8581(17)	61(6)
C37A	5315(10)	5990(30)	9450(20)	63(5)
C38A	5350(18)	6980(30)	9977(17)	61(6)
C39A	5046(15)	7690(20)	9816(17)	61(5)
C40A	5039(14)	8123(15)	9017(11)	58(5)
C41A	4655(10)	6640(30)	8575(17)	61(5)
C42A	4956(16)	5510(30)	9556(19)	65(6)
C43A	4661(17)	7140(50)	9973(17)	61(6)
C44A	4631(9)	6260(30)	9400(20)	64(5)
C1A	3801(8)	7940(20)	7360(20)	39(4)
C2A	3990(10)	8520(30)	8082(14)	43(5)
C3A	3893(10)	8360(30)	8760(30)	43(5)
C4A	3616(10)	7660(30)	8940(30)	43(5)
C5A	3450(10)	7160(30)	8383(18)	42(5)
C6A	3550(6)	7310(18)	7538(15)	37(4)
C7A	3367(9)	6520(30)	7040(13)	34(4)
C8A	2985(7)	6694(18)	6804(12)	35(4)
C9A	2799(10)	5930(30)	6419(16)	37(5)
C10A	2959(8)	4960(20)	6234(15)	39(4)
C11A	3325(10)	4880(30)	6487(18)	39(5)
C12A	3531(7)	5580(20)	6868(14)	39(4)
C13A	2765(7)	7620(20)	7016(14)	36(5)
C14A	2475(8)	7400(30)	7612(19)	41(7)
C15A	2604(9)	8160(20)	6326(19)	37(6)
C16A	2769(7)	4140(20)	5783(18)	42(5)
C17A	2359(7)	4250(30)	5750(30)	50(7)
C18A	2939(12)	3950(30)	5007(17)	49(8)
C19A	3897(7)	5260(20)	7193(15)	45(5)
C20A	3864(11)	4730(40)	7960(20)	53(8)
C21A	4132(10)	4700(30)	6620(20)	48(8)
C22A	3818(11)	9815(16)	6640(30)	44(4)
C23A	3403(8)	9950(30)	6800(30)	43(5)
C24A	3302(12)	11020(30)	7020(30)	44(5)
C25A	3428(12)	11800(40)	6480(30)	46(6)
C26A	3855(13)	11710(40)	6330(30)	46(6)

C27A	3950(13)	10612(17)	6100(30)	48(5)
C28A	3664(10)	7970(30)	5665(18)	37(4)
C29A	3791(11)	6920(30)	5330(20)	43(5)
C30A	3508(11)	6540(30)	4790(30)	37(5)
C31A	3462(11)	7240(30)	4130(20)	37(5)
C32A	3354(9)	8280(30)	4400(30)	35(5)
C33A	3605(10)	8760(30)	4996(16)	37(5)
Os1B	5386(2)	8663(5)	6249(4)	72(2)
P1B	6036(3)	8925(8)	6480(6)	36(2)
O1B	5268(4)	9890(20)	6955(19)	59(5)
O2B	4651(4)	9843(19)	6810(20)	56(5)
O3B	5452(12)	6630(20)	5480(30)	93(11)
C45B	5467(7)	7450(20)	5730(30)	76(6)
O4B	5390(13)	9850(40)	4778(17)	79(11)
C46B	5394(7)	9400(40)	5353(17)	68(6)
C34B	4944(3)	10269(19)	7061(12)	60(5)
C35B	4919(6)	11310(20)	7520(20)	71(5)
C36B	5043(13)	12151(17)	6953(15)	78(6)
C37B	5053(15)	13180(20)	7360(20)	77(6)
C38B	4702(13)	13340(20)	7830(30)	76(7)
C39B	4654(14)	12580(30)	8450(30)	73(6)
C40B	4635(12)	11450(20)	7990(20)	72(6)
C41B	5318(13)	11190(30)	8060(30)	74(6)
C42B	5382(13)	13090(30)	7990(30)	75(7)
C43B	5010(20)	12450(30)	8940(20)	77(6)
C44B	5332(14)	12200(30)	8460(30)	75(6)
C1B	6195(8)	8450(20)	7430(30)	44(4)
C2B	5987(10)	9050(30)	8096(14)	48(5)
C3B	6080(11)	8880(30)	8790(30)	49(6)
C4B	6355(11)	8190(30)	8990(30)	48(6)
C5B	6528(11)	7690(30)	8483(19)	48(5)
C6B	6439(6)	7840(20)	7607(16)	50(5)
C7B	6650(11)	7060(30)	7152(16)	53(5)
C8B	7032(8)	7320(20)	6926(15)	54(5)
C9B	7224(14)	6590(40)	6480(20)	58(6)
C10B	7095(13)	5690(30)	6234(19)	59(5)

C11B	6718(13)	5460(40)	6470(20)	58(6)
C12B	6504(8)	6130(20)	6914(17)	56(5)
C13B	7235(8)	8250(20)	7206(16)	55(6)
C14B	7506(12)	8020(30)	7830(20)	59(9)
C15B	7413(12)	8850(30)	6570(20)	57(9)
C16B	7317(10)	4930(30)	5783(17)	63(6)
C17B	7490(11)	4120(30)	6290(20)	59(8)
C18B	7101(14)	4420(40)	5150(20)	66(9)
C19B	6138(9)	5750(30)	7200(18)	58(6)
C20B	6160(13)	5210(40)	7960(20)	59(9)
C21B	5927(11)	5160(40)	6610(30)	63(9)
C22B	6179(11)	10286(16)	6640(30)	42(4)
C23B	6584(9)	10480(30)	6770(30)	46(5)
C24B	6670(13)	11580(40)	6960(30)	50(6)
C25B	6546(13)	12300(40)	6390(30)	49(6)
C26B	6121(12)	12220(40)	6290(30)	47(6)
C27B	6027(12)	11057(18)	6050(30)	45(5)
C28B	6353(10)	8410(30)	5720(20)	40(4)
C29B	6226(12)	7360(30)	5380(20)	44(5)
C30B	6488(13)	7050(40)	4810(30)	49(6)
C31B	6561(14)	7680(40)	4140(30)	49(6)
C32B	6672(12)	8740(30)	4460(30)	46(6)
C33B	6417(11)	9210(40)	5036(17)	42(5)

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Table 3.14. Bond lengths [Å] and angles [°] for **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**.

Os1-C50	1.852(12)	C12-C19	1.50(2)
Os1-C51	1.866(11)	C13-C15	1.55(3)
Os1-O1	2.139(10)	C13-C14	1.56(3)
Os1-O2	2.166(9)	C13-H13	1.00
Os1-P1	2.429(4)	C14-H14A	0.98
Os1-Os1#1	2.7820(10)	C14-H14B	0.98
P1-C28	1.837(15)	C14-H14C	0.98
P1-C1	1.868(16)	C15-H15A	0.98
P1-C22	1.872(14)	C15-H15B	0.98
O1-C34	1.267(13)	C15-H15C	0.98
O2-C42	1.259(13)	C16-C17	1.42(4)
O3-C50	1.154(12)	C16-C18	1.53(4)
O4-C51	1.160(12)	C16-H16	1.00
C1-C2	1.38(2)	C17-H17A	0.98
C1-C6	1.43(2)	C17-H17B	0.98
C2-C3	1.41(2)	C17-H17C	0.98
C2-H2	0.95	C18-H18A	0.98
C3-C4	1.38(2)	C18-H18B	0.98
C3-H3	0.95	C18-H18C	0.98
C4-C5	1.42(3)	C19-C21	1.55(2)
C4-H4	0.95	C19-C20	1.58(2)
C5-C6	1.37(3)	C19-H19	1.00
C5-H5	0.95	C20-H20A	0.98
C6-C7	1.52(2)	C20-H20B	0.98
C7-C8	1.38(3)	C20-H20C	0.98
C7-C12	1.41(2)	C21-H21A	0.98
C8-C9	1.43(3)	C21-H21B	0.98
C8-C13	1.50(3)	C21-H21C	0.98
C9-C10	1.36(3)	C22-C27	1.53(2)
C9-H9	0.95	C22-C23	1.55(2)
C10-C11	1.38(3)	C22-H22	1.00
C10-C16	1.56(3)	C23-C24	1.57(2)
C11-C12	1.41(3)	C23-H23A	0.99
C11-H11	0.95	C23-H23B	0.99

C24-C25	1.54(3)	C37-C38	1.52(2)
C24-H24A	0.99	C37-C41	1.541(19)
C24-H24B	0.99	C37-H37	1.00
C25-C26	1.49(3)	C38-C39	1.54(2)
C25-H25A	0.99	C38-H38A	0.99
C25-H25B	0.99	C38-H38B	0.99
C26-C27	1.535(19)	C39-C38#1	1.54(2)
C26-H26A	0.99	C39-C40	1.54(3)
C26-H26B	0.99	C39-H39	1.00
C27-H27A	0.99	C40-H40A	0.99
C27-H27B	0.99	C40-H40B	0.99
C28-C29	1.53(2)	C41-C37#1	1.541(19)
C28-C33	1.54(2)	C41-H41A	0.99
C28-H28	1.00	C41-H41B	0.99
C29-C30	1.53(2)	C42-O2#1	1.259(13)
C29-H29A	0.99	C42-C43	1.52(2)
C29-H29B	0.99	C43-C48	1.52(3)
C30-C31	1.54(3)	C43-C44#1	1.550(17)
C30-H30A	0.99	C43-C44	1.551(16)
C30-H30B	0.99	C44-C45	1.58(2)
C31-C32	1.50(3)	C44-H44A	0.99
C31-H31A	0.99	C44-H44B	0.99
C31-H31B	0.99	C45-C49	1.51(2)
C32-C33	1.54(2)	C45-C46	1.52(2)
C32-H32A	0.99	C45-H45	1.00
C32-H32B	0.99	C46-C47	1.53(2)
C33-H33A	0.99	C46-H46A	0.99
C33-H33B	0.99	C46-H46B	0.99
C34-O1#1	1.267(13)	C47-C46#1	1.53(2)
C34-C35	1.54(2)	C47-C48	1.56(3)
C35-C40	1.52(3)	C47-H47	1.00
C35-C36	1.550(17)	C48-H48A	0.99
C35-C36#1	1.550(17)	C48-H48B	0.99
C36-C37	1.52(2)	C49-C45#1	1.51(2)
C36-H36A	0.99	C49-H49A	0.99
C36-H36B	0.99	C49-H49B	0.99

Os1A-C45A	1.79(2)	C42A-H42A	0.99
Os1A-C46A	1.86(2)	C42A-H42B	0.99
Os1A-O1A	2.066(17)	C43A-C44A	1.52(6)
Os1A-O2B	2.122(17)	C43A-H43A	0.99
Os1A-P1A	2.424(9)	C43A-H43B	0.99
Os1A-Os1B	2.794(3)	C44A-H44C	1.00
P1A-C1A	1.80(4)	C1A-C6A	1.27(4)
P1A-C28A	1.882(14)	C1A-C2A	1.62(5)
P1A-C22A	1.887(14)	C2A-C3A	1.24(5)
O1A-C34A	1.30(2)	C2A-H2A	0.95
O2A-C34A	1.29(2)	C3A-C4A	1.40(6)
O2A-Os1B	2.089(17)	C3A-H3A	0.95
O3A-C45A	1.182(14)	C4A-C5A	1.32(5)
O4A-C46A	1.148(15)	C4A-H4A	0.95
C34A-C35A	1.57(3)	C5A-C6A	1.53(4)
C35A-C36A	1.36(3)	C5A-H5A	0.95
C35A-C41A	1.55(3)	C6A-C7A	1.508(14)
C35A-C40A	1.66(3)	C7A-C12A	1.40(4)
C36A-C37A	1.64(4)	C7A-C8A	1.47(4)
C36A-H36C	0.99	C8A-C9A	1.39(5)
C36A-H36D	0.99	C8A-C13A	1.505(14)
C37A-C42A	1.46(6)	C9A-C10A	1.43(5)
C37A-C38A	1.59(6)	C9A-H9A	0.95
C37A-H37A	1.00	C10A-C11A	1.41(5)
C38A-C39A	1.47(7)	C10A-C16A	1.500(14)
C38A-H38C	0.99	C11A-C12A	1.36(5)
C38A-H38D	0.99	C11A-H11A	0.95
C39A-C40A	1.50(4)	C12A-C19A	1.504(14)
C39A-C43A	1.60(7)	C13A-C15A	1.507(14)
C39A-H39A	1.00	C13A-C14A	1.508(14)
C40A-H40C	0.99	C13A-H13A	1.00
C40A-H40D	0.99	C14A-H14D	0.98
C41A-C44A	1.53(4)	C14A-H14E	0.98
C41A-H41C	0.99	C14A-H14F	0.98
C41A-H41D	0.99	C15A-H15D	0.98
C42A-C44A	1.56(6)	C15A-H15E	0.98

C15A-H15F	0.98	C28A-C29A	1.56(5)
C16A-C17A	1.499(14)	C28A-C33A	1.58(5)
C16A-C18A	1.504(14)	C28A-H28A	1.00
C16A-H16A	1.00	C29A-C30A	1.48(5)
C17A-H17D	0.98	C29A-H29C	0.99
C17A-H17E	0.98	C29A-H29D	0.99
C17A-H17F	0.98	C30A-C31A	1.46(6)
C18A-H18D	0.98	C30A-H30C	0.99
C18A-H18E	0.98	C30A-H30D	0.99
C18A-H18F	0.98	C31A-C32A	1.50(5)
C19A-C21A	1.505(14)	C31A-H31C	0.99
C19A-C20A	1.506(14)	C31A-H31D	0.99
C19A-H19A	1.00	C32A-C33A	1.51(5)
C20A-H20D	0.98	C32A-H32C	0.99
C20A-H20E	0.98	C32A-H32D	0.99
C20A-H20F	0.98	C33A-H33C	0.99
C21A-H21D	0.98	C33A-H33D	0.99
C21A-H21E	0.98	Os1B-C46B	1.83(2)
C21A-H21F	0.98	Os1B-C45B	1.86(2)
C22A-C27A	1.49(5)	Os1B-O1B	2.065(18)
C22A-C23A	1.55(5)	Os1B-P1B	2.424(9)
C22A-H22A	1.00	P1B-C1B	1.86(5)
C23A-C24A	1.50(5)	P1B-C22B	1.879(14)
C23A-H23C	0.99	P1B-C28B	1.884(14)
C23A-H23D	0.99	O1B-C34B	1.30(2)
C24A-C25A	1.46(6)	O2B-C34B	1.28(2)
C24A-H24C	0.99	O3B-C45B	1.156(15)
C24A-H24D	0.99	O4B-C46B	1.158(14)
C25A-C26A	1.58(6)	C34B-C35B	1.58(3)
C25A-H25C	0.99	C35B-C40B	1.34(3)
C25A-H25D	0.99	C35B-C36B	1.55(4)
C26A-C27A	1.54(6)	C35B-C41B	1.74(5)
C26A-H26C	0.99	C36B-C37B	1.52(4)
C26A-H26D	0.99	C36B-H36E	0.99
C27A-H27C	0.99	C36B-H36F	0.99
C27A-H27D	0.99	C37B-C38B	1.53(6)

C37B-C42B	1.63(6)	C9B-H9B	0.95
C37B-H37B	1.00	C10B-C11B	1.46(7)
C38B-C39B	1.48(6)	C10B-C16B	1.505(14)
C38B-H38E	0.99	C11B-C12B	1.41(6)
C38B-H38F	0.99	C11B-H11B	0.95
C39B-C43B	1.57(9)	C12B-C19B	1.502(14)
C39B-C40B	1.68(4)	C13B-C15B	1.502(14)
C39B-H39B	1.00	C13B-C14B	1.503(14)
C40B-H40E	0.99	C13B-H13B	1.00
C40B-H40F	0.99	C14B-H14G	0.98
C41B-C44B	1.50(6)	C14B-H14H	0.98
C41B-H41E	0.99	C14B-H14I	0.98
C41B-H41F	0.99	C15B-H15G	0.98
C42B-C44B	1.44(7)	C15B-H15H	0.98
C42B-H42C	0.99	C15B-H15I	0.98
C42B-H42D	0.99	C16B-C18B	1.503(14)
C43B-C44B	1.46(10)	C16B-C17B	1.508(14)
C43B-H43C	0.99	C16B-H16B	1.00
C43B-H43D	0.99	C17B-H17G	0.98
C44B-H44D	1.00	C17B-H17H	0.98
C1B-C6B	1.23(4)	C17B-H17I	0.98
C1B-C2B	1.60(5)	C18B-H18G	0.98
C2B-C3B	1.28(5)	C18B-H18H	0.98
C2B-H2B	0.95	C18B-H18I	0.98
C3B-C4B	1.39(6)	C19B-C20B	1.499(14)
C3B-H3B	0.95	C19B-C21B	1.502(14)
C4B-C5B	1.27(6)	C19B-H19B	1.00
C4B-H4B	0.95	C20B-H20G	0.98
C5B-C6B	1.57(4)	C20B-H20H	0.98
C5B-H5B	0.95	C20B-H20I	0.98
C6B-C7B	1.498(14)	C21B-H21G	0.98
C7B-C12B	1.40(5)	C21B-H21H	0.98
C7B-C8B	1.48(5)	C21B-H21I	0.98
C8B-C9B	1.42(6)	C22B-C23B	1.51(5)
C8B-C13B	1.501(14)	C22B-C27B	1.54(5)
C9B-C10B	1.34(6)	C22B-H22B	1.00

C23B-C24B	1.51(5)	C28B-H28B	1.00
C23B-H23E	0.99	C29B-C30B	1.43(5)
C23B-H23F	0.99	C29B-H29E	0.99
C24B-C25B	1.45(7)	C29B-H29F	0.99
C24B-H24E	0.99	C30B-C31B	1.46(6)
C24B-H24F	0.99	C30B-H30E	0.99
C25B-C26B	1.56(6)	C30B-H30F	0.99
C25B-H25E	0.99	C31B-C32B	1.55(6)
C25B-H25F	0.99	C31B-H31E	0.99
C26B-C27B	1.62(5)	C31B-H31F	0.99
C26B-H26E	0.99	C32B-C33B	1.49(5)
C26B-H26F	0.99	C32B-H32E	0.99
C27B-H27E	0.99	C32B-H32F	0.99
C27B-H27F	0.99	C33B-H33E	0.99
C28B-C29B	1.57(5)	C33B-H33F	0.99
C28B-C33B	1.60(5)		

C50-Os1-C51	92.5(6)	C1-P1-Os1	113.6(5)
C50-Os1-O1	90.3(5)	C22-P1-Os1	112.6(5)
C51-Os1-O1	176.1(5)	C34-O1-Os1	124.3(10)
C50-Os1-O2	171.9(5)	C42-O2-Os1	123.2(9)
C51-Os1-O2	93.8(5)	C2-C1-C6	118.4(14)
O1-Os1-O2	83.2(4)	C2-C1-P1	110.2(11)
C50-Os1-P1	98.1(4)	C6-C1-P1	131.3(12)
C51-Os1-P1	90.7(5)	C1-C2-C3	123.3(14)
O1-Os1-P1	91.6(3)	C1-C2-H2	118.3
O2-Os1-P1	86.9(3)	C3-C2-H2	118.3
C50-Os1-Os1#1	91.4(4)	C4-C3-C2	117.9(16)
C51-Os1-Os1#1	94.3(4)	C4-C3-H3	121.0
O1-Os1-Os1#1	82.9(3)	C2-C3-H3	121.0
O2-Os1-Os1#1	83.1(3)	C3-C4-C5	119.0(18)
P1-Os1-Os1#1	169.06(10)	C3-C4-H4	120.5
C28-P1-C1	109.6(7)	C5-C4-H4	120.5
C28-P1-C22	105.1(7)	C6-C5-C4	122.9(18)
C1-P1-C22	96.5(7)	C6-C5-H5	118.6
C28-P1-Os1	117.1(6)	C4-C5-H5	118.6

C5-C6-C1	118.0(16)	C13-C15-H15C	109.5
C5-C6-C7	114.1(14)	H15A-C15-H15C	109.5
C1-C6-C7	127.8(15)	H15B-C15-H15C	109.5
C8-C7-C12	121.4(16)	C17-C16-C18	120(3)
C8-C7-C6	120.6(16)	C17-C16-C10	120(3)
C12-C7-C6	117.3(15)	C18-C16-C10	113(2)
C7-C8-C9	118.0(17)	C17-C16-H16	99.3
C7-C8-C13	122.2(16)	C18-C16-H16	99.3
C9-C8-C13	119.8(16)	C10-C16-H16	99.3
C10-C9-C8	121.3(19)	C16-C17-H17A	109.5
C10-C9-H9	119.3	C16-C17-H17B	109.5
C8-C9-H9	119.3	H17A-C17-H17B	109.5
C9-C10-C11	120.1(19)	C16-C17-H17C	109.5
C9-C10-C16	123(2)	H17A-C17-H17C	109.5
C11-C10-C16	117(2)	H17B-C17-H17C	109.5
C10-C11-C12	120.7(19)	C16-C18-H18A	109.5
C10-C11-H11	119.6	C16-C18-H18B	109.5
C12-C11-H11	119.6	H18A-C18-H18B	109.5
C11-C12-C7	118.4(17)	C16-C18-H18C	109.5
C11-C12-C19	119.8(16)	H18A-C18-H18C	109.5
C7-C12-C19	121.8(15)	H18B-C18-H18C	109.5
C8-C13-C15	111.7(18)	C12-C19-C21	114.4(15)
C8-C13-C14	109.6(16)	C12-C19-C20	107.3(15)
C15-C13-C14	109.9(17)	C21-C19-C20	110.1(15)
C8-C13-H13	108.5	C12-C19-H19	108.3
C15-C13-H13	108.5	C21-C19-H19	108.3
C14-C13-H13	108.5	C20-C19-H19	108.3
C13-C14-H14A	109.5	C19-C20-H20A	109.5
C13-C14-H14B	109.5	C19-C20-H20B	109.5
H14A-C14-H14B	109.5	H20A-C20-H20B	109.5
C13-C14-H14C	109.5	C19-C20-H20C	109.5
H14A-C14-H14C	109.5	H20A-C20-H20C	109.5
H14B-C14-H14C	109.5	H20B-C20-H20C	109.5
C13-C15-H15A	109.5	C19-C21-H21A	109.5
C13-C15-H15B	109.5	C19-C21-H21B	109.5
H15A-C15-H15B	109.5	H21A-C21-H21B	109.5

C19-C21-H21C	109.5	C22-C27-H27B	109.4
H21A-C21-H21C	109.5	C26-C27-H27B	109.4
H21B-C21-H21C	109.5	H27A-C27-H27B	108.0
C27-C22-C23	112.4(13)	C29-C28-C33	105.9(13)
C27-C22-P1	117.1(10)	C29-C28-P1	111.6(11)
C23-C22-P1	111.5(10)	C33-C28-P1	116.0(11)
C27-C22-H22	104.8	C29-C28-H28	107.6
C23-C22-H22	104.8	C33-C28-H28	107.6
P1-C22-H22	104.8	P1-C28-H28	107.6
C22-C23-C24	111.3(14)	C30-C29-C28	113.9(14)
C22-C23-H23A	109.4	C30-C29-H29A	108.8
C24-C23-H23A	109.4	C28-C29-H29A	108.8
C22-C23-H23B	109.4	C30-C29-H29B	108.8
C24-C23-H23B	109.4	C28-C29-H29B	108.8
H23A-C23-H23B	108.0	H29A-C29-H29B	107.7
C25-C24-C23	110.2(16)	C29-C30-C31	107.6(15)
C25-C24-H24A	109.6	C29-C30-H30A	110.2
C23-C24-H24A	109.6	C31-C30-H30A	110.2
C25-C24-H24B	109.6	C29-C30-H30B	110.2
C23-C24-H24B	109.6	C31-C30-H30B	110.2
H24A-C24-H24B	108.1	H30A-C30-H30B	108.5
C26-C25-C24	111.7(16)	C32-C31-C30	111.9(18)
C26-C25-H25A	109.3	C32-C31-H31A	109.2
C24-C25-H25A	109.3	C30-C31-H31A	109.2
C26-C25-H25B	109.3	C32-C31-H31B	109.2
C24-C25-H25B	109.3	C30-C31-H31B	109.2
H25A-C25-H25B	107.9	H31A-C31-H31B	107.9
C25-C26-C27	113.0(13)	C31-C32-C33	110.9(15)
C25-C26-H26A	109.0	C31-C32-H32A	109.5
C27-C26-H26A	109.0	C33-C32-H32A	109.5
C25-C26-H26B	109.0	C31-C32-H32B	109.5
C27-C26-H26B	109.0	C33-C32-H32B	109.5
H26A-C26-H26B	107.8	H32A-C32-H32B	108.0
C22-C27-C26	111.0(15)	C28-C33-C32	112.9(14)
C22-C27-H27A	109.4	C28-C33-H33A	109.0
C26-C27-H27A	109.4	C32-C33-H33A	109.0

C28-C33-H33B	109.0	C35-C40-C39	109.0(15)
C32-C33-H33B	109.0	C35-C40-H40A	109.9
H33A-C33-H33B	107.8	C39-C40-H40A	109.9
O1#1-C34-O1	125.6(17)	C35-C40-H40B	109.9
O1#1-C34-C35	117.1(8)	C39-C40-H40B	109.9
O1-C34-C35	117.1(8)	H40A-C40-H40B	108.3
C40-C35-C34	106.8(15)	C37-C41-C37#1	109.3(17)
C40-C35-C36	110.6(11)	C37-C41-H41A	109.8
C34-C35-C36	109.8(11)	C37#1-C41-H41A	109.8
C40-C35-C36#1	110.6(11)	C37-C41-H41B	109.8
C34-C35-C36#1	109.8(11)	C37#1-C41-H41B	109.8
C36-C35-C36#1	109.1(16)	H41A-C41-H41B	108.3
C37-C36-C35	108.7(13)	O2#1-C42-O2	127.5(16)
C37-C36-H36A	109.9	O2#1-C42-C43	116.2(8)
C35-C36-H36A	109.9	O2-C42-C43	116.2(8)
C37-C36-H36B	109.9	C48-C43-C42	105.7(16)
C35-C36-H36B	109.9	C48-C43-C44#1	110.7(11)
H36A-C36-H36B	108.3	C42-C43-C44#1	109.4(10)
C36-C37-C38	109.3(13)	C48-C43-C44	110.7(11)
C36-C37-C41	110.4(14)	C42-C43-C44	109.4(10)
C38-C37-C41	108.3(15)	C44#1-C43-C44	110.7(16)
C36-C37-H37	109.6	C43-C44-C45	108.4(12)
C38-C37-H37	109.6	C43-C44-H44A	110.0
C41-C37-H37	109.6	C45-C44-H44A	110.0
C37-C38-C39	111.7(14)	C43-C44-H44B	110.0
C37-C38-H38A	109.3	C45-C44-H44B	110.0
C39-C38-H38A	109.3	H44A-C44-H44B	108.4
C37-C38-H38B	109.3	C49-C45-C46	110.5(16)
C39-C38-H38B	109.3	C49-C45-C44	107.5(15)
H38A-C38-H38B	107.9	C46-C45-C44	106.4(14)
C38-C39-C38#1	107.6(19)	C49-C45-H45	110.8
C38-C39-C40	108.5(12)	C46-C45-H45	110.8
C38#1-C39-C40	108.5(12)	C44-C45-H45	110.8
C38-C39-H39	110.7	C45-C46-C47	111.6(16)
C38#1-C39-H39	110.7	C45-C46-H46A	109.3
C40-C39-H39	110.7	C47-C46-H46A	109.3

C45-C46-H46B	109.3	O2B-Os1A-Os1B	81.2(4)
C47-C46-H46B	109.3	P1A-Os1A-Os1B	167.4(4)
H46A-C46-H46B	108.0	C1A-P1A-C28A	108.2(17)
C46#1-C47-C46	111(2)	C1A-P1A-C22A	96.9(18)
C46#1-C47-C48	108.3(14)	C28A-P1A-C22A	106.2(19)
C46-C47-C48	108.3(14)	C1A-P1A-Os1A	117.5(10)
C46#1-C47-H47	109.8	C28A-P1A-Os1A	116.5(14)
C46-C47-H47	109.8	C22A-P1A-Os1A	109.1(13)
C48-C47-H47	109.8	C34A-O1A-Os1A	124.9(15)
C43-C48-C47	107.6(19)	C34A-O2A-Os1B	125.4(15)
C43-C48-H48A	110.2	O3A-C45A-Os1A	177(4)
C47-C48-H48A	110.2	O4A-C46A-Os1A	173(4)
C43-C48-H48B	110.2	O2A-C34A-O1A	123(3)
C47-C48-H48B	110.2	O2A-C34A-C35A	118.8(15)
H48A-C48-H48B	108.5	O1A-C34A-C35A	117.8(14)
C45-C49-C45#1	114(2)	C36A-C35A-C41A	115(3)
C45-C49-H49A	108.8	C36A-C35A-C34A	117(2)
C45#1-C49-H49A	108.8	C41A-C35A-C34A	106.9(16)
C45-C49-H49B	108.8	C36A-C35A-C40A	112.2(19)
C45#1-C49-H49B	108.8	C41A-C35A-C40A	102.6(19)
H49A-C49-H49B	107.7	C34A-C35A-C40A	101.2(17)
O3-C50-Os1	175.1(14)	C35A-C36A-C37A	113(2)
O4-C51-Os1	176.4(13)	C35A-C36A-H36C	109.0
C45A-Os1A-C46A	93.3(17)	C37A-C36A-H36C	109.0
C45A-Os1A-O1A	87.6(17)	C35A-C36A-H36D	109.0
C46A-Os1A-O1A	176.5(9)	C37A-C36A-H36D	109.0
C45A-Os1A-O2B	175.6(15)	H36C-C36A-H36D	107.8
C46A-Os1A-O2B	90.2(18)	C42A-C37A-C38A	111(3)
O1A-Os1A-O2B	88.9(15)	C42A-C37A-C36A	108(3)
C45A-Os1A-P1A	95.3(7)	C38A-C37A-C36A	102(2)
C46A-Os1A-P1A	92.1(7)	C42A-C37A-H37A	112.0
O1A-Os1A-P1A	91.3(5)	C38A-C37A-H37A	112.0
O2B-Os1A-P1A	87.3(5)	C36A-C37A-H37A	112.0
C45A-Os1A-Os1B	95.9(8)	C39A-C38A-C37A	110(3)
C46A-Os1A-Os1B	93.0(7)	C39A-C38A-H38C	109.6
O1A-Os1A-Os1B	83.5(4)	C37A-C38A-H38C	109.6

C39A-C38A-H38D	109.6	C43A-C44A-H44C	109.5
C37A-C38A-H38D	109.6	C41A-C44A-H44C	109.5
H38C-C38A-H38D	108.1	C42A-C44A-H44C	109.5
C38A-C39A-C40A	115(4)	C6A-C1A-C2A	115(4)
C38A-C39A-C43A	110(2)	C6A-C1A-P1A	134(3)
C40A-C39A-C43A	108(4)	C2A-C1A-P1A	110(2)
C38A-C39A-H39A	107.7	C3A-C2A-C1A	122(4)
C40A-C39A-H39A	107.7	C3A-C2A-H2A	119.1
C43A-C39A-H39A	107.7	C1A-C2A-H2A	119.1
C39A-C40A-C35A	105.1(16)	C2A-C3A-C4A	122(4)
C39A-C40A-H40C	110.7	C2A-C3A-H3A	118.9
C35A-C40A-H40C	110.7	C4A-C3A-H3A	118.9
C39A-C40A-H40D	110.7	C5A-C4A-C3A	120(4)
C35A-C40A-H40D	110.7	C5A-C4A-H4A	120.2
H40C-C40A-H40D	108.8	C3A-C4A-H4A	120.2
C44A-C41A-C35A	109(3)	C4A-C5A-C6A	122(4)
C44A-C41A-H41C	109.8	C4A-C5A-H5A	119.0
C35A-C41A-H41C	109.8	C6A-C5A-H5A	119.0
C44A-C41A-H41D	109.8	C1A-C6A-C7A	129(3)
C35A-C41A-H41D	109.8	C1A-C6A-C5A	120(3)
H41C-C41A-H41D	108.3	C7A-C6A-C5A	111(2)
C37A-C42A-C44A	112(2)	C12A-C7A-C8A	119(2)
C37A-C42A-H42A	109.1	C12A-C7A-C6A	123(3)
C44A-C42A-H42A	109.1	C8A-C7A-C6A	118(3)
C37A-C42A-H42B	109.1	C9A-C8A-C7A	119(3)
C44A-C42A-H42B	109.1	C9A-C8A-C13A	117(3)
H42A-C42A-H42B	107.9	C7A-C8A-C13A	124(2)
C44A-C43A-C39A	107(3)	C8A-C9A-C10A	124(3)
C44A-C43A-H43A	110.3	C8A-C9A-H9A	118.2
C39A-C43A-H43A	110.3	C10A-C9A-H9A	118.2
C44A-C43A-H43B	110.3	C11A-C10A-C9A	112(3)
C39A-C43A-H43B	110.3	C11A-C10A-C16A	123(3)
H43A-C43A-H43B	108.5	C9A-C10A-C16A	125(3)
C43A-C44A-C41A	111(3)	C12A-C11A-C10A	128(3)
C43A-C44A-C42A	108(4)	C12A-C11A-H11A	115.8
C41A-C44A-C42A	109(3)	C10A-C11A-H11A	115.8

C11A-C12A-C7A	118(3)	C16A-C18A-H18F	109.5
C11A-C12A-C19A	119(3)	H18D-C18A-H18F	109.5
C7A-C12A-C19A	123(2)	H18E-C18A-H18F	109.5
C8A-C13A-C15A	112.8(15)	C21A-C19A-C12A	113.1(15)
C8A-C13A-C14A	112.6(14)	C21A-C19A-C20A	113(3)
C15A-C13A-C14A	111(2)	C12A-C19A-C20A	112.8(15)
C8A-C13A-H13A	106.5	C21A-C19A-H19A	105.7
C15A-C13A-H13A	106.5	C12A-C19A-H19A	105.7
C14A-C13A-H13A	106.5	C20A-C19A-H19A	105.7
C13A-C14A-H14D	109.5	C19A-C20A-H20D	109.5
C13A-C14A-H14E	109.5	C19A-C20A-H20E	109.5
H14D-C14A-H14E	109.5	H20D-C20A-H20E	109.5
C13A-C14A-H14F	109.5	C19A-C20A-H20F	109.5
H14D-C14A-H14F	109.5	H20D-C20A-H20F	109.5
H14E-C14A-H14F	109.5	H20E-C20A-H20F	109.5
C13A-C15A-H15D	109.5	C19A-C21A-H21D	109.5
C13A-C15A-H15E	109.5	C19A-C21A-H21E	109.5
H15D-C15A-H15E	109.5	H21D-C21A-H21E	109.5
C13A-C15A-H15F	109.5	C19A-C21A-H21F	109.5
H15D-C15A-H15F	109.5	H21D-C21A-H21F	109.5
H15E-C15A-H15F	109.5	H21E-C21A-H21F	109.5
C17A-C16A-C10A	113.9(15)	C27A-C22A-C23A	110(3)
C17A-C16A-C18A	113(3)	C27A-C22A-P1A	118(3)
C10A-C16A-C18A	113.4(15)	C23A-C22A-P1A	115(2)
C17A-C16A-H16A	105.0	C27A-C22A-H22A	104.1
C10A-C16A-H16A	105.0	C23A-C22A-H22A	104.1
C18A-C16A-H16A	105.0	P1A-C22A-H22A	104.1
C16A-C17A-H17D	109.5	C24A-C23A-C22A	113(3)
C16A-C17A-H17E	109.5	C24A-C23A-H23C	109.0
H17D-C17A-H17E	109.5	C22A-C23A-H23C	109.0
C16A-C17A-H17F	109.5	C24A-C23A-H23D	109.0
H17D-C17A-H17F	109.5	C22A-C23A-H23D	109.0
H17E-C17A-H17F	109.5	H23C-C23A-H23D	107.8
C16A-C18A-H18D	109.5	C25A-C24A-C23A	115(4)
C16A-C18A-H18E	109.5	C25A-C24A-H24C	108.5
H18D-C18A-H18E	109.5	C23A-C24A-H24C	108.5

C25A-C24A-H24D	108.5	C31A-C30A-H30D	109.3
C23A-C24A-H24D	108.5	C29A-C30A-H30D	109.3
H24C-C24A-H24D	107.5	H30C-C30A-H30D	107.9
C24A-C25A-C26A	111(4)	C30A-C31A-C32A	111(4)
C24A-C25A-H25C	109.3	C30A-C31A-H31C	109.5
C26A-C25A-H25C	109.3	C32A-C31A-H31C	109.5
C24A-C25A-H25D	109.3	C30A-C31A-H31D	109.5
C26A-C25A-H25D	109.3	C32A-C31A-H31D	109.5
H25C-C25A-H25D	108.0	H31C-C31A-H31D	108.1
C27A-C26A-C25A	110(4)	C31A-C32A-C33A	116(3)
C27A-C26A-H26C	109.8	C31A-C32A-H32C	108.4
C25A-C26A-H26C	109.8	C33A-C32A-H32C	108.4
C27A-C26A-H26D	109.8	C31A-C32A-H32D	108.4
C25A-C26A-H26D	109.8	C33A-C32A-H32D	108.4
H26C-C26A-H26D	108.2	H32C-C32A-H32D	107.5
C22A-C27A-C26A	115(4)	C32A-C33A-C28A	108(3)
C22A-C27A-H27C	108.5	C32A-C33A-H33C	110.1
C26A-C27A-H27C	108.5	C28A-C33A-H33C	110.1
C22A-C27A-H27D	108.5	C32A-C33A-H33D	110.1
C26A-C27A-H27D	108.5	C28A-C33A-H33D	110.1
H27C-C27A-H27D	107.5	H33C-C33A-H33D	108.4
C29A-C28A-C33A	110(3)	C46B-Os1B-C45B	92.0(17)
C29A-C28A-P1A	114(2)	C46B-Os1B-O1B	96(2)
C33A-C28A-P1A	113(2)	C45B-Os1B-O1B	171.9(18)
C29A-C28A-H28A	106.2	C46B-Os1B-O2A	171.2(18)
C33A-C28A-H28A	106.2	C45B-Os1B-O2A	96.0(18)
P1A-C28A-H28A	106.2	O1B-Os1B-O2A	76.2(15)
C30A-C29A-C28A	109(3)	C46B-Os1B-P1B	92.9(7)
C30A-C29A-H29C	109.9	C45B-Os1B-P1B	92.8(7)
C28A-C29A-H29C	109.9	O1B-Os1B-P1B	89.6(5)
C30A-C29A-H29D	109.9	O2A-Os1B-P1B	90.1(5)
C28A-C29A-H29D	109.9	C46B-Os1B-Os1A	93.9(7)
H29C-C29A-H29D	108.3	C45B-Os1B-Os1A	93.2(7)
C31A-C30A-C29A	112(3)	O1B-Os1B-Os1A	83.6(4)
C31A-C30A-H30C	109.3	O2A-Os1B-Os1A	82.3(4)
C29A-C30A-H30C	109.3	P1B-Os1B-Os1A	170.8(4)

C1B-P1B-C22B	96.3(17)	H38E-C38B-H38F	107.8
C1B-P1B-C28B	108.2(18)	C38B-C39B-C43B	111(4)
C22B-P1B-C28B	106(2)	C38B-C39B-C40B	105(3)
C1B-P1B-Os1B	113.8(10)	C43B-C39B-C40B	101(3)
C22B-P1B-Os1B	115.3(13)	C38B-C39B-H39B	112.7
C28B-P1B-Os1B	115.4(14)	C43B-C39B-H39B	112.7
C34B-O1B-Os1B	125.1(15)	C40B-C39B-H39B	112.7
C34B-O2B-Os1A	125.9(15)	C35B-C40B-C39B	113(3)
O3B-C45B-Os1B	166(4)	C35B-C40B-H40E	109.1
O4B-C46B-Os1B	178(4)	C39B-C40B-H40E	109.1
O2B-C34B-O1B	123(3)	C35B-C40B-H40F	109.1
O2B-C34B-C35B	119.9(15)	C39B-C40B-H40F	109.1
O1B-C34B-C35B	117.4(14)	H40E-C40B-H40F	107.8
C40B-C35B-C36B	121(2)	C44B-C41B-C35B	101(3)
C40B-C35B-C34B	119(2)	C44B-C41B-H41E	111.5
C36B-C35B-C34B	106(2)	C35B-C41B-H41E	111.5
C40B-C35B-C41B	109(3)	C44B-C41B-H41F	111.5
C36B-C35B-C41B	99(2)	C35B-C41B-H41F	111.5
C34B-C35B-C41B	98.3(19)	H41E-C41B-H41F	109.3
C37B-C36B-C35B	110(2)	C44B-C42B-C37B	110(3)
C37B-C36B-H36E	109.6	C44B-C42B-H42C	109.6
C35B-C36B-H36E	109.6	C37B-C42B-H42C	109.6
C37B-C36B-H36F	109.6	C44B-C42B-H42D	109.6
C35B-C36B-H36F	109.6	C37B-C42B-H42D	109.6
H36E-C36B-H36F	108.2	H42C-C42B-H42D	108.1
C36B-C37B-C38B	111(3)	C44B-C43B-C39B	112(3)
C36B-C37B-C42B	106(3)	C44B-C43B-H43C	109.2
C38B-C37B-C42B	105(3)	C39B-C43B-H43C	109.2
C36B-C37B-H37B	111.6	C44B-C43B-H43D	109.2
C38B-C37B-H37B	111.6	C39B-C43B-H43D	109.2
C42B-C37B-H37B	111.6	H43C-C43B-H43D	107.9
C39B-C38B-C37B	113(3)	C42B-C44B-C43B	104(5)
C39B-C38B-H38E	109.0	C42B-C44B-C41B	117(5)
C37B-C38B-H38E	109.0	C43B-C44B-C41B	116(5)
C39B-C38B-H38F	109.0	C42B-C44B-H44D	106.3
C37B-C38B-H38F	109.0	C43B-C44B-H44D	106.3

C41B-C44B-H44D	106.3	C11B-C12B-C19B	118(3)
C6B-C1B-C2B	119(4)	C8B-C13B-C15B	113.4(16)
C6B-C1B-P1B	132(3)	C8B-C13B-C14B	113.3(16)
C2B-C1B-P1B	109(2)	C15B-C13B-C14B	111(3)
C3B-C2B-C1B	118(4)	C8B-C13B-H13B	106.2
C3B-C2B-H2B	120.8	C15B-C13B-H13B	106.2
C1B-C2B-H2B	120.8	C14B-C13B-H13B	106.2
C2B-C3B-C4B	122(5)	C13B-C14B-H14G	109.5
C2B-C3B-H3B	118.8	C13B-C14B-H14H	109.5
C4B-C3B-H3B	118.8	H14G-C14B-H14H	109.5
C5B-C4B-C3B	121(5)	C13B-C14B-H14I	109.5
C5B-C4B-H4B	119.3	H14G-C14B-H14I	109.5
C3B-C4B-H4B	119.3	H14H-C14B-H14I	109.5
C4B-C5B-C6B	121(4)	C13B-C15B-H15G	109.5
C4B-C5B-H5B	119.6	C13B-C15B-H15H	109.5
C6B-C5B-H5B	119.6	H15G-C15B-H15H	109.5
C1B-C6B-C7B	132(3)	C13B-C15B-H15I	109.5
C1B-C6B-C5B	118(3)	H15G-C15B-H15I	109.5
C7B-C6B-C5B	109(2)	H15H-C15B-H15I	109.5
C12B-C7B-C8B	119(3)	C18B-C16B-C10B	113.2(16)
C12B-C7B-C6B	124(3)	C18B-C16B-C17B	109(4)
C8B-C7B-C6B	118(3)	C10B-C16B-C17B	112.7(15)
C9B-C8B-C7B	117(3)	C18B-C16B-H16B	107.1
C9B-C8B-C13B	119(3)	C10B-C16B-H16B	107.1
C7B-C8B-C13B	124(2)	C17B-C16B-H16B	107.1
C10B-C9B-C8B	127(4)	C16B-C17B-H17G	109.5
C10B-C9B-H9B	116.7	C16B-C17B-H17H	109.5
C8B-C9B-H9B	116.7	H17G-C17B-H17H	109.5
C9B-C10B-C11B	115(4)	C16B-C17B-H17I	109.5
C9B-C10B-C16B	124(4)	H17G-C17B-H17I	109.5
C11B-C10B-C16B	121(4)	H17H-C17B-H17I	109.5
C12B-C11B-C10B	123(4)	C16B-C18B-H18G	109.5
C12B-C11B-H11B	118.5	C16B-C18B-H18H	109.5
C10B-C11B-H11B	118.5	H18G-C18B-H18H	109.5
C7B-C12B-C11B	120(3)	C16B-C18B-H18I	109.5
C7B-C12B-C19B	122(2)	H18G-C18B-H18I	109.5

H18H-C18B-H18I	109.5	H24E-C24B-H24F	107.6
C20B-C19B-C21B	112(3)	C24B-C25B-C26B	110(4)
C20B-C19B-C12B	113.5(16)	C24B-C25B-H25E	109.7
C21B-C19B-C12B	113.4(16)	C26B-C25B-H25E	109.7
C20B-C19B-H19B	105.6	C24B-C25B-H25F	109.7
C21B-C19B-H19B	105.6	C26B-C25B-H25F	109.7
C12B-C19B-H19B	105.6	H25E-C25B-H25F	108.2
C19B-C20B-H20G	109.5	C25B-C26B-C27B	108(4)
C19B-C20B-H20H	109.5	C25B-C26B-H26E	110.2
H20G-C20B-H20H	109.5	C27B-C26B-H26E	110.2
C19B-C20B-H20I	109.5	C25B-C26B-H26F	110.2
H20G-C20B-H20I	109.5	C27B-C26B-H26F	110.2
H20H-C20B-H20I	109.5	H26E-C26B-H26F	108.5
C19B-C21B-H21G	109.5	C22B-C27B-C26B	112(3)
C19B-C21B-H21H	109.5	C22B-C27B-H27E	109.3
H21G-C21B-H21H	109.5	C26B-C27B-H27E	109.3
C19B-C21B-H21I	109.5	C22B-C27B-H27F	109.3
H21G-C21B-H21I	109.5	C26B-C27B-H27F	109.3
H21H-C21B-H21I	109.5	H27E-C27B-H27F	107.9
C23B-C22B-C27B	110(3)	C29B-C28B-C33B	110(3)
C23B-C22B-P1B	117(2)	C29B-C28B-P1B	113(2)
C27B-C22B-P1B	115(3)	C33B-C28B-P1B	112(2)
C23B-C22B-H22B	104.3	C29B-C28B-H28B	106.9
C27B-C22B-H22B	104.3	C33B-C28B-H28B	106.9
P1B-C22B-H22B	104.3	P1B-C28B-H28B	106.9
C24B-C23B-C22B	113(3)	C30B-C29B-C28B	108(3)
C24B-C23B-H23E	108.9	C30B-C29B-H29E	110.1
C22B-C23B-H23E	108.9	C28B-C29B-H29E	110.1
C24B-C23B-H23F	108.9	C30B-C29B-H29F	110.1
C22B-C23B-H23F	108.9	C28B-C29B-H29F	110.1
H23E-C23B-H23F	107.7	H29E-C29B-H29F	108.4
C25B-C24B-C23B	114(4)	C29B-C30B-C31B	121(4)
C25B-C24B-H24E	108.7	C29B-C30B-H30E	107.1
C23B-C24B-H24E	108.7	C31B-C30B-H30E	107.1
C25B-C24B-H24F	108.7	C29B-C30B-H30F	107.1
C23B-C24B-H24F	108.7	C31B-C30B-H30F	107.1

H30E-C30B-H30F	106.8	C33B-C32B-H32F	108.2
C30B-C31B-C32B	106(4)	C31B-C32B-H32F	108.2
C30B-C31B-H31E	110.6	H32E-C32B-H32F	107.4
C32B-C31B-H31E	110.6	C32B-C33B-C28B	109(3)
C30B-C31B-H31F	110.6	C32B-C33B-H33E	109.9
C32B-C31B-H31F	110.6	C28B-C33B-H33E	109.9
H31E-C31B-H31F	108.8	C32B-C33B-H33F	109.9
C33B-C32B-C31B	116(4)	C28B-C33B-H33F	109.9
C33B-C32B-H32E	108.2	H33E-C33B-H33F	108
C31B-C32B-H32E	108.2		

Table 3.15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**.. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Os1	21(1)	7(1)	12(1)	1(1)	1(1)	0(1)
P1	23(2)	18(1)	22(2)	4(1)	7(1)	6(1)
O1	26(4)	25(5)	18(4)	8(3)	-2(3)	-1(3)
O2	23(4)	20(4)	18(5)	-12(3)	-6(3)	1(3)
O3	32(6)	9(4)	29(6)	-7(3)	3(4)	-4(3)
O4	41(7)	26(5)	19(4)	12(4)	6(4)	6(4)
C1	20(5)	26(5)	13(4)	1(4)	2(4)	0(4)
C2	19(5)	26(6)	19(5)	-1(4)	1(4)	4(4)
C3	30(6)	32(6)	20(5)	-1(4)	-1(4)	4(5)
C4	36(7)	45(7)	28(6)	4(5)	1(5)	-3(6)
C5	28(6)	35(7)	29(5)	11(5)	2(4)	-1(5)
C6	18(5)	28(5)	29(5)	10(4)	1(4)	-3(4)
C7	29(5)	35(5)	35(6)	5(5)	-4(5)	-4(4)
C8	26(5)	42(6)	38(7)	13(5)	-2(5)	-7(4)
C9	35(6)	57(6)	49(9)	7(6)	-7(6)	-14(5)
C10	41(6)	56(6)	50(7)	3(7)	0(6)	-13(5)
C11	41(6)	45(7)	50(8)	-4(6)	0(5)	-12(5)
C12	34(6)	34(5)	38(7)	3(5)	-1(5)	-4(4)
C13	27(6)	51(7)	61(8)	9(6)	-2(6)	-4(5)
C14	39(9)	64(12)	79(12)	20(9)	16(9)	3(8)
C15	24(8)	64(10)	71(12)	25(8)	1(7)	4(6)
C16	72(9)	87(10)	80(10)	-19(8)	-1(7)	-30(8)
C17	82(11)	106(19)	130(20)	-43(16)	7(10)	-33(10)
C18	65(12)	46(10)	61(10)	1(8)	-14(8)	-9(8)
C19	35(6)	26(6)	40(7)	0(5)	-6(5)	-2(5)
C20	53(10)	37(8)	43(8)	4(6)	-4(7)	-3(7)
C21	50(9)	23(7)	47(8)	5(6)	-1(7)	5(6)
C22	30(6)	22(5)	19(6)	0(4)	1(4)	-1(4)
C23	28(6)	30(6)	34(7)	-1(5)	0(5)	3(4)
C24	40(7)	37(6)	41(7)	-5(5)	6(6)	8(5)

C25	42(6)	27(6)	47(9)	-5(5)	0(6)	9(5)
C26	40(6)	18(5)	44(8)	-1(6)	-4(6)	3(4)
C27	27(6)	19(5)	27(7)	4(4)	0(5)	2(4)
C28	21(6)	29(5)	21(5)	1(4)	-2(4)	1(4)
C29	27(6)	25(5)	28(6)	-2(5)	2(5)	1(4)
C30	44(8)	25(6)	38(7)	-6(5)	-8(6)	-4(5)
C31	39(8)	33(6)	34(7)	-3(5)	-6(6)	0(6)
C32	31(7)	32(6)	28(6)	4(5)	-8(5)	1(5)
C33	34(7)	31(6)	33(6)	1(5)	-4(5)	1(5)
C34	22(6)	11(6)	8(5)	2(5)	0	0
C35	23(7)	15(6)	15(6)	5(5)	0	0
C36	32(6)	16(5)	20(6)	2(4)	3(4)	-7(4)
C37	30(6)	22(5)	22(6)	6(4)	3(4)	-5(4)
C38	43(7)	35(6)	20(6)	1(5)	9(5)	-3(5)
C39	37(8)	18(7)	17(6)	-4(5)	0	0
C40	27(8)	18(6)	18(6)	-2(5)	0	0
C41	40(8)	26(7)	26(8)	5(6)	0	0
C42	13(5)	22(6)	10(6)	-8(5)	0	0
C43	1(5)	27(6)	15(6)	-8(5)	0	0
C44	20(6)	29(6)	23(6)	-9(5)	-5(4)	-1(4)
C45	34(6)	34(6)	19(5)	-3(5)	-2(4)	-4(4)
C46	40(7)	34(7)	32(6)	3(6)	-2(5)	-1(5)
C47	42(9)	37(7)	30(8)	2(6)	0	0
C48	44(9)	35(7)	29(7)	1(6)	0	0
C49	39(8)	46(10)	33(8)	3(7)	0	0
C50	18(6)	22(4)	19(5)	7(4)	4(4)	1(4)
C51	26(6)	17(5)	14(4)	-7(4)	-3(4)	-7(4)
Os1A	16(2)	131(3)	40(2)	2(2)	-2(1)	1(2)
P1A	32(4)	46(4)	43(4)	-4(4)	-1(3)	-4(4)
O1A	30(7)	86(10)	43(7)	-3(7)	2(6)	8(6)
O2A	34(7)	90(10)	42(8)	-4(7)	-2(6)	-5(7)
O3A	6(10)	102(11)	51(14)	-3(10)	6(10)	6(8)
C45A	17(8)	100(8)	41(9)	2(6)	-1(7)	6(6)
O4A	3(9)	108(16)	54(11)	8(11)	-3(8)	-12(10)
C46A	28(9)	98(9)	49(7)	0(7)	0(6)	-4(7)
C34A	34(6)	86(8)	50(6)	-1(6)	1(6)	2(6)

C35A	44(7)	80(7)	54(6)	1(5)	1(6)	-1(6)
C36A	47(8)	79(9)	56(8)	3(7)	1(7)	0(7)
C37A	54(8)	80(8)	57(8)	4(6)	0(7)	-2(7)
C38A	49(8)	77(9)	56(9)	6(7)	0(7)	-1(7)
C39A	49(8)	80(8)	55(7)	4(6)	1(7)	1(7)
C40A	44(9)	75(8)	54(7)	2(6)	2(7)	1(7)
C41A	47(8)	79(9)	56(8)	1(7)	0(6)	0(7)
C42A	54(9)	82(9)	58(9)	4(7)	2(7)	0(7)
C43A	49(8)	79(9)	56(9)	4(7)	1(7)	1(7)
C44A	53(8)	81(8)	56(8)	3(7)	1(6)	2(7)
C1A	32(7)	44(7)	41(6)	-2(5)	0(5)	-1(6)
C2A	38(8)	47(9)	44(7)	-5(6)	-1(6)	0(7)
C3A	38(9)	48(9)	43(8)	-4(7)	0(6)	2(7)
C4A	37(8)	49(9)	42(8)	1(7)	-2(6)	3(7)
C5A	36(8)	50(8)	40(7)	0(6)	0(6)	2(7)
C6A	31(7)	43(7)	38(7)	1(5)	-2(5)	0(6)
C7A	29(6)	39(6)	35(7)	2(5)	3(5)	-3(5)
C8A	29(6)	40(6)	35(7)	3(6)	2(6)	-2(5)
C9A	31(7)	40(7)	40(8)	2(6)	-1(7)	-1(6)
C10A	34(7)	41(7)	43(8)	4(6)	0(6)	1(5)
C11A	34(7)	39(7)	44(8)	1(7)	0(6)	3(6)
C12A	34(6)	41(7)	40(7)	2(6)	4(6)	0(5)
C13A	32(8)	38(8)	39(8)	3(6)	1(7)	-1(6)
C14A	32(11)	51(14)	39(11)	4(10)	1(9)	-1(10)
C15A	31(12)	35(12)	44(11)	4(9)	1(9)	0(10)
C16A	39(8)	41(8)	48(9)	3(7)	-5(7)	2(6)
C17A	39(10)	50(15)	61(15)	2(13)	-7(9)	5(8)
C18A	46(13)	51(15)	51(11)	0(10)	-1(10)	3(12)
C19A	37(8)	52(9)	46(9)	3(8)	2(7)	3(7)
C20A	47(15)	64(16)	49(11)	4(11)	6(10)	7(13)
C21A	41(12)	56(15)	47(12)	8(11)	5(10)	13(11)
C22A	39(7)	47(6)	47(8)	-2(6)	-1(6)	-5(5)
C23A	39(8)	42(8)	49(9)	0(7)	1(7)	-2(6)
C24A	41(8)	42(8)	49(9)	-1(7)	3(7)	-1(7)
C25A	45(9)	44(8)	49(9)	2(7)	2(7)	-3(7)
C26A	43(9)	47(8)	50(10)	2(7)	0(7)	-5(7)

C27A	43(8)	48(8)	51(9)	0(7)	0(7)	-5(6)
C28A	33(7)	39(7)	40(7)	0(6)	-3(6)	-3(6)
C29A	39(8)	42(8)	46(8)	-3(7)	-2(7)	0(7)
C30A	35(9)	35(8)	42(8)	-3(7)	0(7)	1(7)
C31A	33(9)	36(8)	44(8)	-4(7)	-1(7)	1(7)
C32A	32(8)	34(8)	39(8)	-2(7)	-2(7)	0(7)
C33A	32(8)	37(8)	41(8)	-1(6)	-1(7)	-1(7)
Os1B	22(2)	166(4)	28(2)	5(2)	-1(1)	-3(2)
P1B	22(4)	61(5)	26(4)	1(4)	4(3)	5(4)
O1B	25(7)	104(8)	47(9)	3(7)	0(6)	-1(6)
O2B	26(7)	95(8)	47(9)	2(7)	0(6)	-4(6)
O3B	70(20)	137(12)	74(18)	-5(11)	12(16)	-13(11)
C45B	47(9)	131(9)	52(9)	0(7)	2(8)	-4(7)
O4B	70(20)	122(18)	49(11)	2(12)	4(11)	12(15)
C46B	38(9)	122(10)	43(8)	-1(7)	-1(7)	3(8)
C34B	32(7)	96(7)	52(8)	3(6)	1(6)	-3(5)
C35B	58(8)	91(7)	64(7)	-1(6)	-1(6)	-2(6)
C36B	66(9)	94(8)	74(8)	1(6)	0(7)	0(7)
C37B	65(9)	93(8)	74(8)	2(6)	1(7)	0(7)
C38B	64(9)	91(9)	72(9)	3(7)	1(7)	1(7)
C39B	61(8)	87(9)	70(8)	0(7)	2(7)	2(7)
C40B	62(9)	88(9)	66(9)	0(7)	1(7)	2(7)
C41B	61(9)	90(9)	70(9)	0(7)	-1(7)	-2(7)
C42B	63(9)	87(9)	75(9)	0(7)	3(7)	2(7)
C43B	64(8)	93(9)	73(9)	2(7)	-1(7)	1(7)
C44B	62(8)	88(9)	74(8)	-1(7)	-1(7)	0(7)
C1B	37(7)	55(7)	38(6)	2(5)	-1(5)	0(6)
C2B	44(9)	55(9)	46(7)	3(6)	0(6)	2(7)
C3B	45(9)	54(9)	47(8)	3(7)	-2(7)	1(8)
C4B	46(9)	54(9)	45(8)	0(7)	-4(7)	2(8)
C5B	44(9)	53(9)	46(7)	1(6)	-5(6)	3(7)
C6B	45(7)	59(7)	45(7)	0(6)	-4(6)	2(6)
C7B	50(7)	58(7)	50(8)	3(6)	1(6)	2(5)
C8B	51(7)	60(7)	52(8)	5(6)	2(6)	3(6)
C9B	55(8)	62(8)	56(9)	2(7)	5(7)	2(6)
C10B	57(8)	62(8)	59(8)	1(7)	6(7)	2(6)

C11B	57(8)	59(8)	57(9)	1(7)	3(7)	2(6)
C12B	56(7)	58(7)	55(8)	1(6)	1(6)	3(6)
C13B	50(9)	60(9)	54(9)	5(7)	1(7)	4(7)
C14B	57(14)	65(16)	55(13)	7(11)	-4(11)	4(12)
C15B	47(15)	68(14)	57(13)	11(11)	0(11)	3(12)
C16B	61(9)	64(9)	63(10)	2(7)	9(8)	2(7)
C17B	45(13)	67(13)	63(14)	10(11)	25(11)	1(11)
C18B	68(16)	63(15)	66(13)	1(11)	9(12)	1(13)
C19B	57(9)	55(10)	61(10)	0(8)	1(7)	3(7)
C20B	59(16)	54(16)	64(12)	3(11)	1(10)	2(13)
C21B	63(14)	57(16)	69(14)	-3(12)	-1(11)	6(12)
C22B	33(7)	57(6)	37(7)	-1(6)	-1(6)	1(5)
C23B	37(8)	57(8)	46(9)	-1(7)	-4(7)	-1(6)
C24B	42(9)	57(8)	51(9)	0(7)	-7(7)	-3(7)
C25B	43(9)	53(9)	51(9)	-1(8)	-7(7)	-4(7)
C26B	42(9)	53(8)	45(9)	-3(7)	-4(7)	-4(7)
C27B	39(8)	53(8)	43(9)	0(7)	-5(7)	-2(7)
C28B	32(7)	53(7)	34(7)	2(6)	3(6)	0(6)
C29B	37(9)	51(8)	42(8)	0(7)	4(7)	0(7)
C30B	43(9)	56(9)	47(9)	-1(7)	6(7)	0(7)
C31B	45(10)	54(9)	47(9)	-1(7)	8(7)	-1(8)
C32B	43(9)	53(9)	42(9)	-1(7)	8(7)	-1(7)
C33B	38(9)	51(8)	37(8)	1(7)	4(7)	0(7)

Table 3.16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$**.

	x	y	z	U(eq)
H2	810	5838	2722	26
H3	967	6042	1419	33
H4	1451	7155	1102	44
H5	1728	8129	2082	37
H9	2456	8678	4338	56
H11	1576	10518	4268	54
H13	2038	6615	3256	55
H14A	2419	7832	2510	91
H14B	2596	6724	2621	91
H14C	2733	7656	3142	91
H15A	2643	6836	4285	79
H15B	2419	5819	4086	79
H15C	2244	6653	4649	79
H16	2165	11167	4499	96
H17A	2692	11403	4644	160
H17B	2720	10283	4285	160
H17C	2756	10442	5195	160
H18A	2082	10221	5918	86
H18B	1802	10967	5485	86
H18C	2183	11399	5811	86
H19	980	8764	3317	40
H20A	1290	10639	2713	66
H20B	911	10158	2420	66
H20C	1290	9575	2263	66
H21A	878	9725	4490	60
H21B	628	10117	3791	60
H21C	988	10740	4034	60
H22	1059	4723	3454	28
H23A	1728	4998	4290	37

H23B	1668	5286	3403	37
H24A	1596	3537	3066	47
H24B	1971	3636	3543	47
H25A	1611	2228	4003	46
H25B	1679	3045	4673	46
H26A	1067	2540	4681	41
H26B	1024	2852	3796	41
H27A	760	4145	4548	29
H27B	1129	4257	5046	29
H28	1596	6829	4650	29
H29A	1179	8225	4791	32
H29B	982	7640	5484	32
H30A	1395	8879	5979	43
H30B	1731	8345	5533	43
H31A	1723	7748	6829	42
H31B	1304	7396	6739	42
H32A	1679	5968	6637	37
H32B	1916	6497	5969	37
H33A	1495	5341	5400	39
H33B	1158	5882	5826	39
H36A	347	9053	2366	27
H36B	571	8057	2106	27
H37	570	9260	1085	30
H38A	565	7518	723	39
H38B	344	8177	101	39
H39	0	6669	402	29
H40A	-221	6462	1703	25
H40B	221	6462	1703	25
H41A	0	9722	484	37
H41B	0	10096	1363	37
H44A	-353	4220	2172	29
H44B	-573	3715	2878	29
H45	-571	2528	1786	35
H46A	-360	1104	2499	42
H46B	-567	1869	3073	42
H47	0	1281	3627	43

H48A	-221	2959	3995	43
H48B	221	2959	3995	43
H49A	0	3114	1274	47
H49B	0	1900	1352	47
H36C	5561	6859	8518	73
H36D	5326	5919	8200	73
H37A	5521	5498	9542	76
H38C	5344	6776	10526	73
H38D	5588	7317	9875	73
H39A	5067	8269	10185	73
H40C	5257	8556	8926	69
H40D	4815	8538	8937	69
H41C	4462	7162	8482	73
H41D	4614	6071	8213	73
H42A	4937	5243	10088	78
H42B	4935	4920	9200	78
H43A	4652	6876	10507	74
H43B	4456	7622	9899	74
H44C	4392	5898	9480	76
H2A	4180	9002	7986	51
H3A	4012	8716	9162	51
H4A	3547	7552	9461	51
H5A	3262	6683	8512	50
H9A	2551	6049	6269	44
H11A	3444	4247	6378	47
H13A	2941	8115	7257	44
H14D	2316	6851	7430	61
H14E	2327	8017	7700	61
H14F	2593	7199	8095	61
H15D	2798	8289	5949	55
H15E	2493	8803	6488	55
H15F	2414	7723	6094	55
H16A	2814	3497	6080	51
H17D	2260	4230	6279	75
H17E	2254	3688	5454	75
H17F	2296	4899	5513	75

H18D	2952	4592	4720	74
H18E	2789	3459	4720	74
H18F	3187	3674	5073	74
H19A	4031	5912	7304	54
H20D	3770	5202	8343	80
H20E	4106	4473	8114	80
H20F	3693	4150	7905	80
H21D	4047	3989	6587	72
H21E	4388	4705	6797	72
H21F	4114	5023	6119	72
H22A	3938	9996	7142	53
H23C	3263	9751	6337	52
H23D	3330	9488	7225	52
H24C	3031	11066	7057	53
H24D	3406	11170	7531	53
H25C	3372	12484	6699	55
H25D	3293	11735	5990	55
H26C	3926	12185	5908	56
H26D	3993	11907	6796	56
H27C	3844	10473	5585	57
H27D	4220	10553	6053	57
H28A	3417	7846	5898	45
H29C	4029	6999	5062	51
H29D	3825	6422	5755	51
H30C	3580	5863	4598	45
H30D	3271	6475	5063	45
H31C	3270	6966	3786	45
H31D	3695	7279	3842	45
H32C	3103	8246	4623	42
H32D	3343	8740	3951	42
H33C	3493	9391	5202	44
H33D	3843	8938	4758	44
H36E	5290	11987	6750	93
H36F	4870	12184	6513	93
H37B	5096	13749	6993	93
H38E	4709	14031	8065	91

H38F	4487	13313	7484	91
H39B	4432	12710	8776	87
H40E	4632	10897	8381	87
H40F	4403	11412	7697	87
H41E	5300	10617	8431	88
H41F	5536	11083	7727	88
H42C	5622	13049	7724	90
H42D	5384	13705	8322	90
H43C	5063	13096	9218	92
H43D	4976	11909	9325	92
H44D	5548	12172	8817	89
H2B	5798	9528	7976	58
H3B	5956	9243	9193	59
H4B	6414	8095	9521	58
H5B	6714	7226	8635	58
H9B	7469	6759	6334	69
H11B	6613	4830	6312	69
H13B	7045	8703	7439	66
H14G	7373	7834	8306	89
H14H	7659	8618	7930	89
H14I	7663	7445	7678	89
H15G	7613	8447	6346	86
H15H	7511	9484	6780	86
H15I	7230	9000	6174	86
H16B	7522	5310	5532	75
H17G	7596	3589	5965	88
H17H	7301	3827	6624	88
H17I	7683	4434	6603	88
H18G	6873	4141	5365	99
H18H	7248	3869	4928	99
H18I	7042	4923	4753	99
H19B	5989	6380	7299	70
H20G	6253	4517	7876	89
H20H	5915	5179	8190	89
H20I	6327	5579	8301	89
H21G	5931	5521	6117	95

H21H	5673	5073	6780	95
H21I	6041	4485	6545	95
H22B	6058	10482	7131	51
H23E	6667	10042	7205	56
H23F	6723	10274	6310	56
H24E	6555	11751	7460	60
H24F	6940	11648	7023	60
H25E	6668	12160	5888	59
H25F	6613	13002	6547	59
H26E	6034	12696	5887	56
H26F	5996	12392	6779	56
H27E	5757	10975	6006	54
H27F	6135	10914	5535	54
H28B	6597	8294	5967	48
H29E	6212	6845	5798	52
H29F	5979	7427	5148	52
H30E	6409	6374	4624	59
H30F	6725	6951	5082	59
H31E	6339	7740	3813	58
H31F	6763	7390	3828	58
H32E	6918	8682	4700	55
H32F	6695	9222	4022	55
H33E	6180	9375	4788	50
H33F	6525	9842	5243	50

Figure 3.4. View of complex 1 of **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

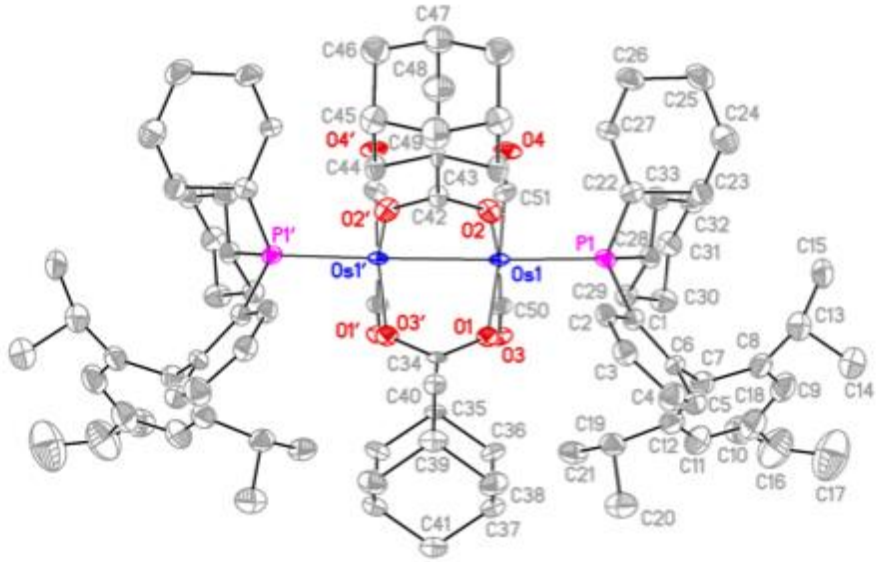
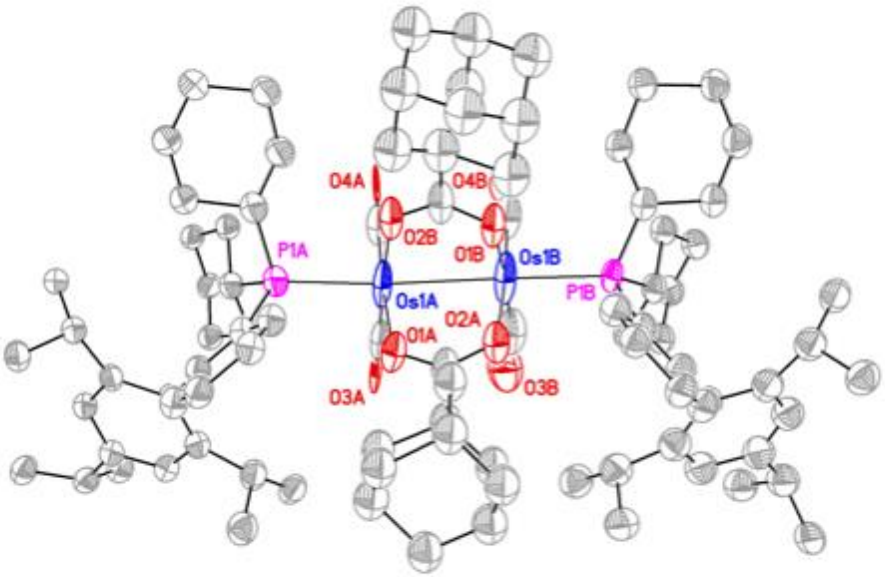


Figure 3.5. View of complex **$Os_2(CO)_4(O_2CR)_2(XPhos)_2$** showing the heteroatom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **$C_{22}H_{28}SO_4Br_2$**:

Crystals grew as very thin, colorless needles by vapor diffusion with chloroform and hexanes. The data crystal was cut from a longer needle and had approximate dimensions; 0.24 x 0.023 x 0.017 mm. The data were collected using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 575 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 5 seconds per frame with a detector offset of +/- 42.2° and 20 seconds per frame with a detector offset of +/- 107.9°. The data were collected at 100 K. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed.The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atom attached to O1 was observed in a ΔF map and refined with an isotropic displacement parameter.

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma (F_O))^2 + (0.0476*P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_w(F^2)$ refined to 0.165, with R(F) equal to 0.0666 and a goodness of fit, S, = 1.01. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[1] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[2] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Empirical formula	C22 H28 Br2 O4 S	
Formula weight	548.32	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.8411(7) Å	α□= 90°.
	b = 15.530(3) Å	β□= 95.069(9)°.
	c = 25.512(2) Å	γ = 90°.
Volume	2305.2(6) $Å^3$	
Z	4	
Density (calculated)	1.580 Mg/m^3	
Absorption coefficient	5.515 mm^{-1}	
F(000)	1112	
Crystal size	0.240 x 0.023 x 0.017 mm^3	
Theta range for data collection	3.335 to 74.479°.	
Index ranges	-6<=h<=7, -17<=k<=19, -31<=l<=20	
Reflections collected	7883	
Independent reflections	4466 [R(int) = 0.0818]	
Completeness to theta = 67.684°	99.2 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.464	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4466 / 0 / 268	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1391	
R indices (all data)	R1 = 0.1218, wR2 = 0.1651	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.859 and -1.012 $e.Å^{-3}$	

Table 3.17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **$C_{22}H_{28}SO_4Br_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

_	x	y	z	U(eq)
C1	5008(12)	9438(5)	3352(3)	26(2)
C2	6762(12)	9415(5)	3016(3)	29(2)
C3	6546(13)	9844(5)	2534(3)	32(2)
C4	4623(12)	10334(5)	2393(3)	28(2)
C5	2898(12)	10389(5)	2731(3)	31(2)
C6	3065(12)	9950(5)	3202(3)	26(2)
C7	5137(12)	8996(5)	3889(3)	27(2)
C8	6693(13)	8196(5)	3916(3)	29(2)
C9	6942(13)	7767(5)	4462(3)	32(2)
C10	8885(13)	7114(5)	4539(3)	33(2)
C11	9181(12)	6735(5)	5091(3)	29(2)
C12	11335(13)	6177(5)	5189(3)	33(2)
C13	11610(15)	5806(6)	5745(3)	40(2)
C14	13771(16)	5253(7)	5841(4)	53(2)
C15	5770(15)	7540(6)	3500(3)	39(2)
C16	5850(12)	9686(5)	4307(3)	26(2)
C17	7420(11)	11579(5)	3950(2)	23(1)
C18	8258(12)	11662(5)	3462(3)	27(2)
C19	7068(13)	12173(5)	3079(3)	31(2)
C20	5060(12)	12582(5)	3204(3)	29(2)
C21	4263(13)	12508(5)	3689(3)	31(2)
C22	5402(12)	11999(5)	4074(3)	28(2)
Br1	4294(2)	10916(1)	1742(1)	44(1)
Br2	3412(2)	13246(1)	2674(1)	44(1)
O1	2811(10)	8770(4)	3975(2)	35(1)
O2	8203(8)	9968(3)	4224(2)	24(1)
O3	11280(8)	10958(4)	4386(2)	28(1)
O4	7963(8)	11045(4)	4921(2)	28(1)
S1	8859(3)	10901(1)	4424(1)	21(1)

Table 3.18. Bond lengths [Å] and angles [°] for **$C_{22}H_{28}SO_4Br_2$**.

C1-C2	1.393(10)	C12-H12B	0.99
C1-C6	1.411(10)	C13-C14	1.528(12)
C1-C7	1.528(10)	C13-H13A	0.99
C2-C3	1.395(10)	C13-H13B	0.99
C2-H2	0.95	C14-H14A	0.98
C3-C4	1.378(11)	C14-H14B	0.98
C3-H3	0.95	C14-H14C	0.98
C4-C5	1.385(10)	C15-H15A	0.98
C4-Br1	1.885(7)	C15-H15B	0.98
C5-C6	1.377(10)	C15-H15C	0.98
C5-H5	0.95	C16-O2	1.476(8)
C6-H6	0.95	C16-H16A	0.99
C7-O1	1.439(9)	C16-H16B	0.99
C7-C8	1.537(11)	C17-C18	1.383(9)
C7-C16	1.543(9)	C17-C22	1.408(10)
C8-C15	1.535(10)	C17-S1	1.759(7)
C8-C9	1.540(10)	C18-C19	1.397(10)
C8-H8	1.00	C18-H18	0.95
C9-C10	1.521(11)	C19-C20	1.395(11)
C9-H9A	0.99	C19-H19	0.95
C9-H9B	0.99	C20-C21	1.364(11)
C10-C11	1.523(10)	C20-Br2	1.894(7)
C10-H10A	0.99	C21-C22	1.385(10)
C10-H10B	0.99	C21-H21	0.95
C11-C12	1.531(11)	C22-H22	0.95
C11-H11A	0.99	O1-H1O	0.64(10)
C11-H11B	0.99	O2-S1	1.572(5)
C12-C13	1.526(10)	O3-S1	1.429(5)
C12-H12A	0.99	O4-S1	1.433(5)

C2-C1-C6	117.7(7)	C3-C2-H2	119.4
C2-C1-C7	124.0(7)	C1-C2-H2	119.5
C6-C1-C7	118.1(6)	C4-C3-C2	120.1(7)
C3-C2-C1	121.1(7)	C4-C3-H3	120.0

C2-C3-H3	120.0	C12-C11-H11A	108.9
C3-C4-C5	119.6(7)	C10-C11-H11B	108.9
C3-C4-Br1	120.7(6)	C12-C11-H11B	108.9
C5-C4-Br1	119.7(6)	H11A-C11-H11B	107.7
C6-C5-C4	120.9(7)	C13-C12-C11	112.5(7)
C6-C5-H5	119.6	C13-C12-H12A	109.1
C4-C5-H5	119.6	C11-C12-H12A	109.1
C5-C6-C1	120.6(7)	C13-C12-H12B	109.1
C5-C6-H6	119.7	C11-C12-H12B	109.1
C1-C6-H6	119.7	H12A-C12-H12B	107.8
O1-C7-C1	105.9(6)	C12-C13-C14	112.2(8)
O1-C7-C8	111.0(6)	C12-C13-H13A	109.2
C1-C7-C8	112.6(6)	C14-C13-H13A	109.2
O1-C7-C16	105.4(6)	C12-C13-H13B	109.2
C1-C7-C16	107.2(6)	C14-C13-H13B	109.2
C8-C7-C16	114.1(6)	H13A-C13-H13B	107.9
C15-C8-C7	109.7(6)	C13-C14-H14A	109.5
C15-C8-C9	109.7(7)	C13-C14-H14B	109.5
C7-C8-C9	113.5(6)	H14A-C14-H14B	109.5
C15-C8-H8	107.9	C13-C14-H14C	109.5
C7-C8-H8	107.9	H14A-C14-H14C	109.5
C9-C8-H8	107.9	H14B-C14-H14C	109.5
C10-C9-C8	114.5(6)	C8-C15-H15A	109.5
C10-C9-H9A	108.6	C8-C15-H15B	109.5
C8-C9-H9A	108.6	H15A-C15-H15B	109.5
C10-C9-H9B	108.6	C8-C15-H15C	109.5
C8-C9-H9B	108.6	H15A-C15-H15C	109.5
H9A-C9-H9B	107.6	H15B-C15-H15C	109.5
C9-C10-C11	113.5(7)	O2-C16-C7	107.7(5)
C9-C10-H10A	108.9	O2-C16-H16A	110.2
C11-C10-H10A	108.9	C7-C16-H16A	110.2
C9-C10-H10B	108.9	O2-C16-H16B	110.2
C11-C10-H10B	108.9	C7-C16-H16B	110.2
H10A-C10-H10B	107.7	H16A-C16-H16B	108.5
C10-C11-C12	113.2(6)	C18-C17-C22	121.9(6)
C10-C11-H11A	108.9	C18-C17-S1	119.2(5)

C22-C17-S1	118.8(5)	C22-C21-H21	119.7
C17-C18-C19	119.3(6)	C21-C22-C17	117.7(7)
C17-C18-H18	120.4	C21-C22-H22	121.2
C19-C18-H18	120.4	C17-C22-H22	121.2
C20-C19-C18	118.4(7)	C7-O1-H1O	118(10)
C20-C19-H19	120.8	C16-O2-S1	115.5(4)
C18-C19-H19	120.8	O3-S1-O4	119.5(3)
C21-C20-C19	122.0(7)	O3-S1-O2	104.4(3)
C21-C20-Br2	120.0(6)	O4-S1-O2	109.5(3)
C19-C20-Br2	118.0(5)	O3-S1-C17	109.4(3)
C20-C21-C22	120.7(7)	O4-S1-C17	109.0(3)
C20-C21-H21	119.6	O2-S1-C17	103.9(3)

Table 3.19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **$C_{22}H_{28}SO_4Br_2$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	26(3)	29(4)	22(3)	-8(3)	3(3)	-5(3)
C2	25(4)	32(4)	30(4)	-1(3)	5(3)	1(3)
C3	30(4)	39(4)	28(3)	2(3)	8(3)	4(3)
C4	25(4)	28(4)	31(4)	0(3)	5(3)	-4(3)
C5	24(4)	33(4)	37(4)	-4(3)	3(3)	0(3)
C6	27(4)	31(4)	22(3)	-1(3)	5(3)	-3(3)
C7	23(3)	26(4)	32(3)	-2(3)	5(3)	-7(3)
C8	32(4)	28(4)	27(3)	-3(3)	1(3)	-3(3)
C9	34(4)	36(4)	24(3)	-7(3)	-5(3)	6(3)
C10	34(4)	28(4)	37(4)	6(3)	4(3)	4(3)
C11	33(4)	24(4)	30(3)	-4(3)	6(3)	-4(3)
C12	36(4)	27(4)	37(4)	1(3)	6(3)	-3(3)
C13	45(5)	34(5)	40(4)	12(4)	4(3)	-8(4)
C14	47(5)	50(6)	60(6)	16(5)	-3(4)	2(5)
C15	46(5)	40(5)	28(4)	-5(4)	-5(3)	-1(4)
C16	23(3)	27(4)	28(3)	-3(3)	3(3)	-3(3)
C17	21(3)	25(4)	23(3)	0(3)	2(2)	-2(3)
C18	21(3)	32(4)	30(3)	4(3)	4(3)	4(3)
C19	34(4)	35(4)	23(3)	2(3)	6(3)	-3(3)
C20	27(4)	33(4)	25(3)	5(3)	-7(3)	-2(3)
C21	29(4)	25(4)	37(4)	4(3)	-1(3)	-3(3)
C22	21(3)	28(4)	35(4)	4(3)	4(3)	-2(3)
Br1	53(1)	47(1)	32(1)	11(1)	8(1)	6(1)
Br2	38(1)	45(1)	48(1)	21(1)	-8(1)	2(1)
O1	26(3)	47(4)	33(3)	-1(3)	4(2)	-7(2)
O2	23(2)	21(2)	27(2)	-1(2)	0(2)	-1(2)
O3	20(2)	35(3)	30(2)	1(2)	2(2)	0(2)
O4	31(3)	37(3)	16(2)	-1(2)	8(2)	0(2)
S1	18(1)	25(1)	21(1)	-1(1)	1(1)	-2(1)

Table 3.20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **$C_{22}H_{28}SO_4Br_2$**.

	x	y	z	U(eq)
H2	8127	9102	3117	35
H3	7727	9799	2302	38
H5	1582	10733	2637	37
H6	1862	9993	3428	32
H8	8256	8380	3829	35
H9A	7201	8221	4733	38
H9B	5479	7475	4520	38
H10A	10339	7396	4462	40
H10B	8583	6640	4282	40
H11A	7813	6383	5149	35
H11B	9261	7211	5350	35
H12A	11254	5698	4932	40
H12B	12705	6528	5131	40
H13A	10246	5452	5803	48
H13B	11685	6285	6002	48
H14A	13721	4786	5582	79
H14B	13844	5009	6196	79
H14C	15133	5610	5806	79
H15A	4204	7372	3566	58
H15B	6761	7029	3519	58
H15C	5755	7798	3149	58
H16A	4780	10181	4270	31
H16B	5808	9443	4665	31
H18	9629	11374	3389	33
H19	7612	12241	2742	37
H21	2912	12809	3763	37
H22	4841	11937	4411	34
H1O	2580(180)	8680(80)	4210(40)	50(40)

Table 3.21. Torsion angles [°] for **$C_{22}H_{28}SO_4Br_2$**.

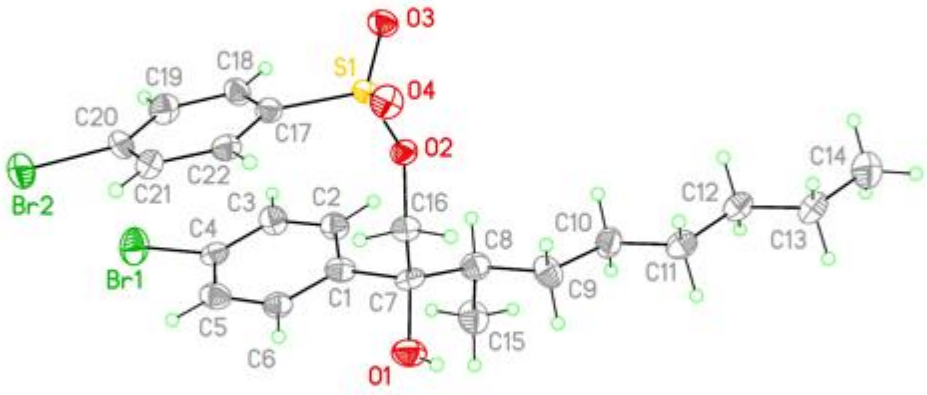
C6-C1-C2-C3	-3.6(11)	C10-C11-C12-C13	179.7(7)
C7-C1-C2-C3	-179.0(7)	C11-C12-C13-C14	-179.7(7)
C1-C2-C3-C4	3.1(12)	O1-C7-C16-O2	-177.9(6)
C2-C3-C4-C5	-0.7(12)	C1-C7-C16-O2	-65.3(7)
C2-C3-C4-Br1	-179.8(6)	C8-C7-C16-O2	60.1(8)
C3-C4-C5-C6	-1.0(11)	C22-C17-C18-C19	-0.3(11)
Br1-C4-C5-C6	178.2(6)	S1-C17-C18-C19	177.5(6)
C4-C5-C6-C1	0.3(11)	C17-C18-C19-C20	-0.2(11)
C2-C1-C6-C5	1.9(10)	C18-C19-C20-C21	1.2(12)
C7-C1-C6-C5	177.6(7)	C18-C19-C20-Br2	-178.1(6)
C2-C1-C7-O1	-149.9(7)	C19-C20-C21-C22	-1.8(12)
C6-C1-C7-O1	34.6(9)	Br2-C20-C21-C22	177.6(6)
C2-C1-C7-C8	-28.4(10)	C20-C21-C22-C17	1.2(11)
C6-C1-C7-C8	156.2(6)	C18-C17-C22-C21	-0.1(11)
C2-C1-C7-C16	97.9(8)	S1-C17-C22-C21	-178.0(5)
C6-C1-C7-C16	-77.5(8)	C7-C16-O2-S1	154.6(4)
O1-C7-C8-C15	58.8(8)	C16-O2-S1-O3	170.1(4)
C1-C7-C8-C15	-59.8(8)	C16-O2-S1-O4	41.0(5)
C16-C7-C8-C15	177.6(6)	C16-O2-S1-C17	-75.3(5)
O1-C7-C8-C9	-64.3(8)	C18-C17-S1-O3	36.7(7)
C1-C7-C8-C9	177.1(6)	C22-C17-S1-O3	-145.4(6)
C16-C7-C8-C9	54.6(8)	C18-C17-S1-O4	169.0(6)
C15-C8-C9-C10	70.8(9)	C22-C17-S1-O4	-13.1(7)
C7-C8-C9-C10	-166.2(6)	C18-C17-S1-O2	-74.3(6)
C8-C9-C10-C11	176.8(6)	C22-C17-S1-O2	103.6(6)
C9-C10-C11-C12	-172.0(7)		

Table 3.22. Hydrogen bonds for **$C_{22}H_{28}SO_4Br_2$** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1O...O4#1	0.64(10)	2.31(10)	2.904(8)	156(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Figure 3.6. View of $C_{22}H_{28}SO_4Br_2$ showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Chapter 4. Diols, α-Ketols and Diones as $2_{2\pi}$ Components in [2+2+2] Cycloadditions of 1,6-Diynes via Ruthenium(0) Catalyzed Transfer Hydrogenation*

4.1 Introduction

Transition metal catalyzed [2+2+2] cycloadditions of π-unsaturated reactants are convergent methods to construct complex (poly)cyclic compounds in an efficient manner.[1] In the event, oxidative cyclometallation to form metal cyclopentadiene complex and intermolecular π-bond insertion event followed by reductive elimination deliver cycloadducts and regenerate the catalyst (Figure 4.1, eq. 1). The use of carbonyl compounds,[2] including carbon dioxide,[3] as $2_{2\pi}$ components in metal catalyzed [2+2+2] cycloaddition can be seen in many precedents,[1-3] wherein carbonyl is insert to form metal-oxygen bond and C-O reductive elimination to form pyrans.[2,3] To our best knowledge, capture of the transient metalacyclopentadiene through an *exo*-type carbonyl addition to form hydroxy-substituted cycloadducts have not been reported.[1-3]

During the exploration of reductive C-C bond forming reactions with carbonyl and various unsaturated compounds via hydrogen transfer,[4] we postulated a pathway for 1,6-diyne-1,2-dione [2+2+2] cycloaddition involving hydrogen transfer from a diol reactant (Figure 4.1, eq. 2). Specifically, ruthenium(0) mediated 1,6-diyne oxidative coupling would provide a ruthenacyclopentadiene complex that participates in successive carbonyl addition with a 1,2-dione to form a ruthenium(II) diolate. Diol or ketol mediated transfer hydrogenolysis of the diolate regenerates zero-valent ruthenium and ketol or dione with release of cycloadduct to close the

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This chapter is based on the published work:

* Sato, H.; Bender, M.; Chen, W.; Krische, M. J. *J. Am. Chem. Soc.* **2016**, *138*, 16244.

catalytic cycle (Figure 4.1, bottom). Herein, we report the first [2+2+2] cycloadditions through *exo*-type carbonyl addition wherein diols, α-detols and diones are incorporated as $2_{2\pi}$ components.[5]

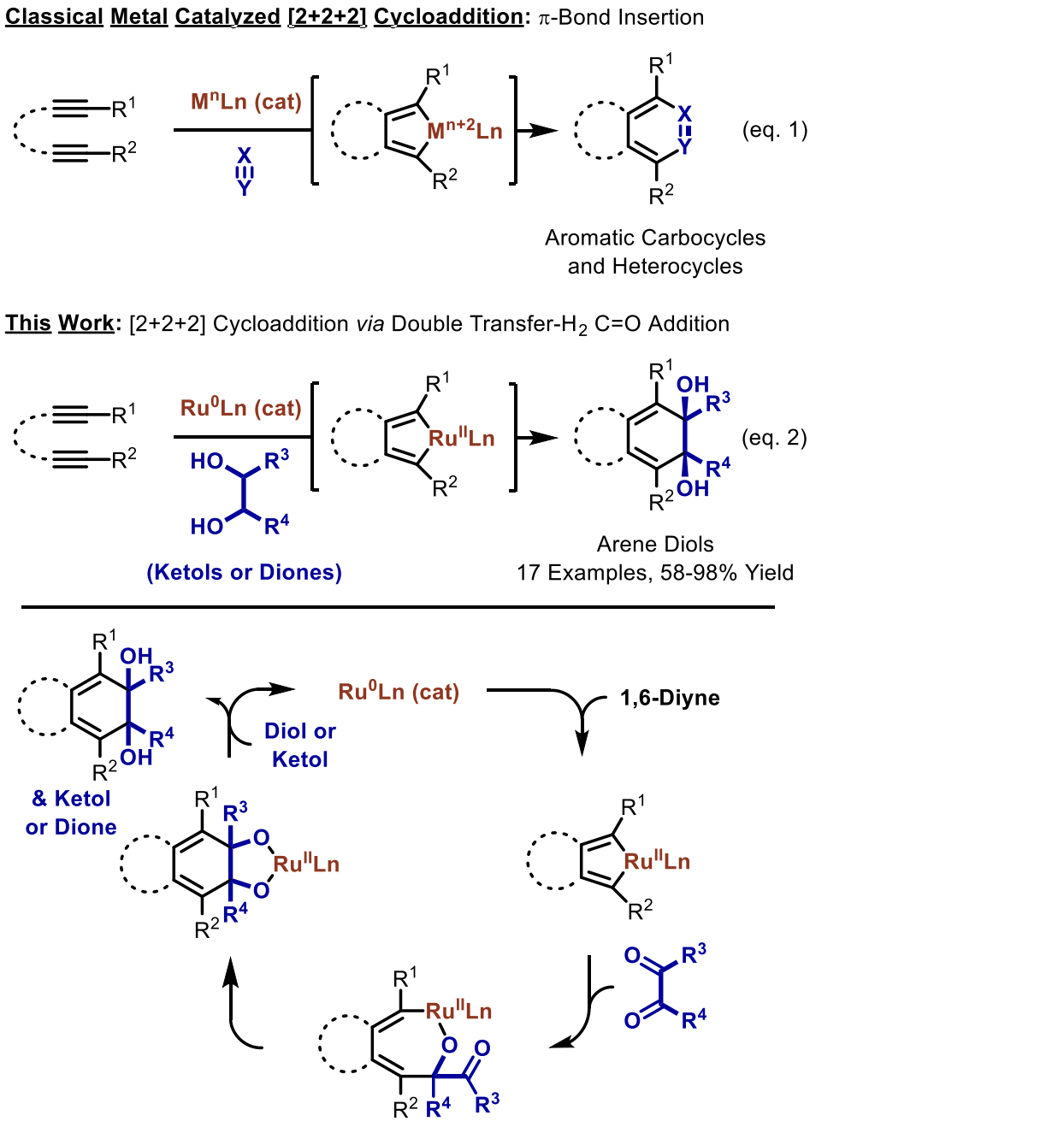
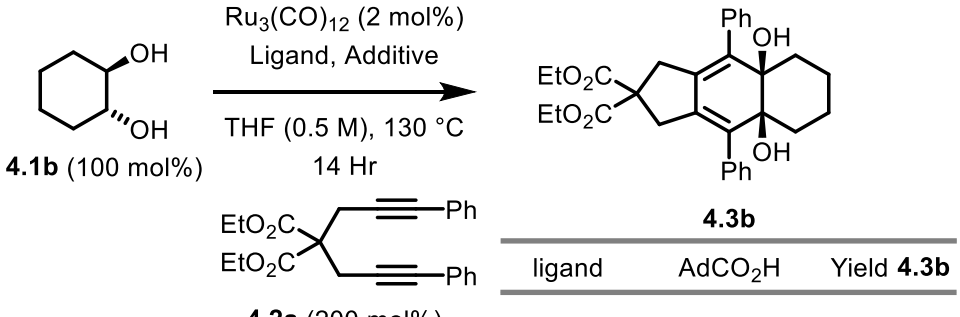


Figure 4.1. Top: Classical vs transfer hydrogenative [2+2+2] cycloaddition using 1,2-diols as $2_{2\pi}$ components. Bottom: General catalytic mechanism.

4.2 Results and Discussion

To explore the feasibility of transfer hydrogenative [2+2+2] cycloaddition, the reaction of *trans*-cyclohexane diol **4.1b** (100 mol%) and 1,6-diyne **4.2a** (200 mol%) were conducted with $Ru_3(CO)_{12}$ (2 mol%) and various phosphine ligands (Scheme 4.1). Only trace amount of the desired product of [2+2+2] cycloaddition **4.3a** were observed using dppe as a ligand. To our delight, carboxylic acid cocatalysts dramatically improved the yield of desired cycloadduct **4.3a**, presumably because acid enhanced the rate and conversion in hydrogenolysis[6] or transfer hydrogenolysis steps[5b] of metalacyclic intermediates. After screening of various acid additive, 1-adamantanecarboxylic acid (6 mol%) was the best as a cocatalyst to give cycloadduct **4.3b** in 92% yield with complete *syn*-diastereoselectivity.



ligand	$AdCO_2H$	Yield **4.3b**
PCy_3 (12 mol%)	---	---
PCy_3 (12 mol%)	(6 mol%)	---
dppe (6 mol%)	---	trace
dppe (6 mol%)	(6 mol%)	92%

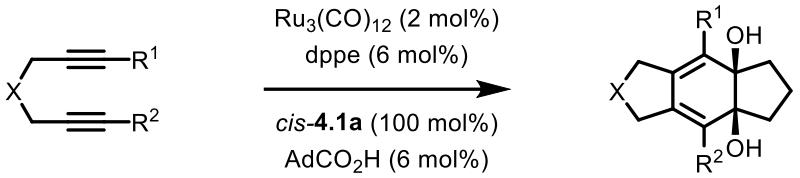
Scheme 4.1. Selected optimization experiments in the [2+2+2] cycloaddition of 1,6-diyne **4.2a** with cyclohexane diol **4.1b**.[a]

To evaluate the generality of the reactions, these optimized conditions were applied to the [2+2+2] cycloaddition of 1,6-diyne **4.2a** with various diols **4.1a**-**4.1i** (Table 4.1). As shown in the table, 5-, 6- and 7-membered cycloalkane diols **4.1a**-**4.1c** participate in cycloaddition to produce bicyclic compounds **4.3a**-**4.3c**. Tolerance of adjacent π-unsaturation is demonstrated by the

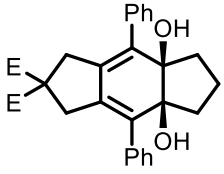
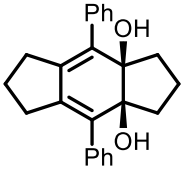
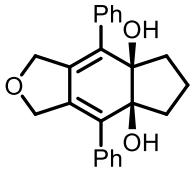
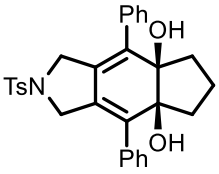
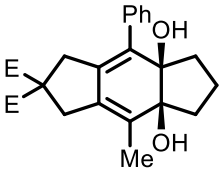
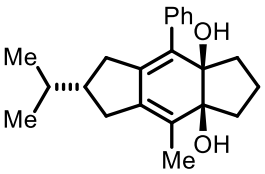
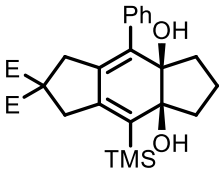
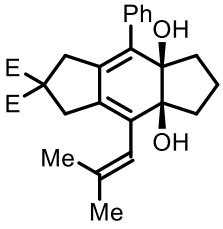
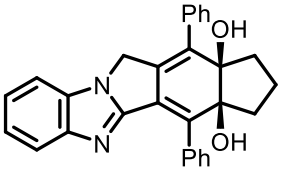
conversion of indane diol **4.1d**, cyclohexene diol **4.1e** and acenaphthalene diol **4.1f** to cycloadducts **4.3d**-**4.3f**, respectively. It is noted that the transient dione derived from cyclohexene diol **4.1e** undergoes cycloaddition more rapidly than tautomerization to form the corresponding catechol. Sugar analogue diol **4.1g** bearing a stereogenic center engages in cycloaddition to form **4.3g** in moderate diastereoselectivity induction. Finally, acyclic vicinal diols, 2,3-butane diol **4.1h** and the diol **4.1i** derived from methyl oleate, are also applicable to the process to give cycloadducts **4.3h** and **4.3i**.

For exploration of diyne scope, various 1,6-diynes **4.2a**-**4.2i** were exposed to cyclopentane diol **4.1a** under the optimal conditions (Table 4.2). As demonstrated by the reaction of diyne **4.2b** to form **4.3j**, the stereochemsitry of the diol substrates *cis*- or *trans*- does not give an effect on the cycloaddition.[7] The formation of cycloadducts **4.3k** and **4.3l** from diynes **4.2c** and **4.2d**, respectively, shows the tolerance of both *O*- and *N*-tethers. The examination of different substituents group at the acetylenic terminus beyond phenyl is illustrated by the cycloaddition of diynes **4.2e**-**4.2h** to form adducts **4.3m**-**4.3p**. Finally, generation of the benzimidazole containing cycloadduct **4.3q** establishes compatibility with *N*-heterocycles. 1,6-Diynes with terminal alkyne and 1,7-diynes do not afford the desired cycloadducts.

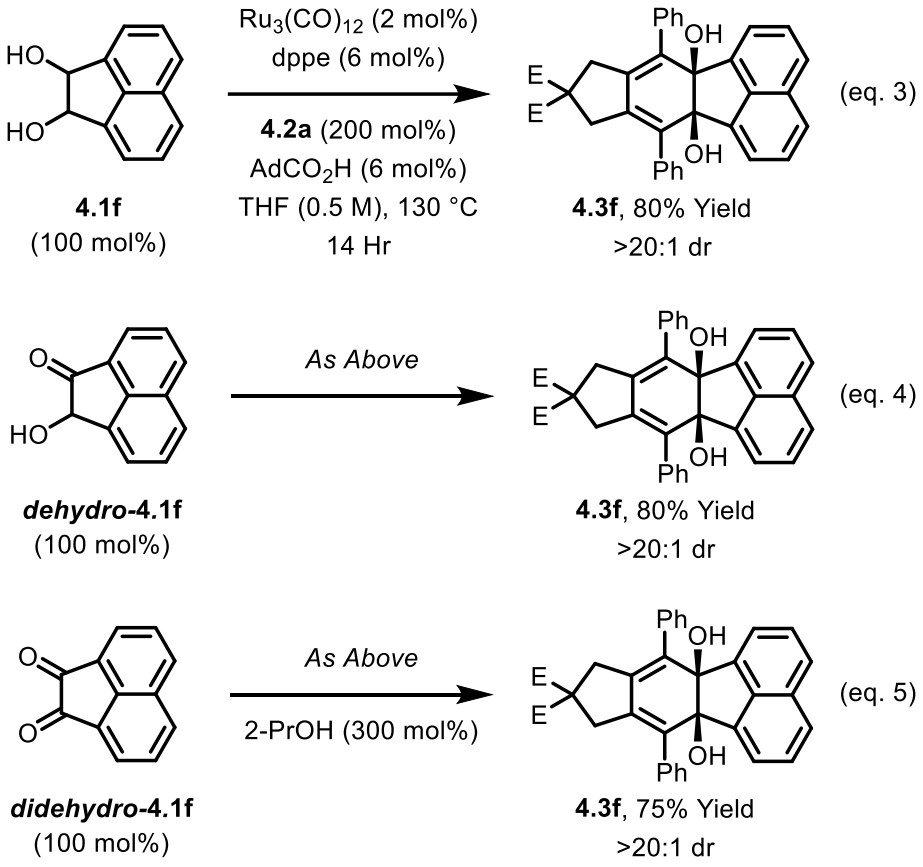
Table 4.2. Survey of diynes **4.2a-4.2i** in ruthenium(0) catalyzed transfer hydrogenative [2+2+2] cycloaddition.[a]



4.2a-i (100 mol%) → **4.3a, j-q**

4.2a, $R^1 = R^2$ = Ph, X = CE_2	**4.2b**, $R^1 = R^2$ = Ph, X = CH_2	**4.2c**, $R^1 = R^2$ = Ph, X = O
4.2d, $R^1 = R^2$ = Ph, X = NTs	**4.2e**, R^1 = Ph, R^2 = Me, X = CE_2	**4.2f**, R^1 = Ph, R^2 = Me, X = CH^iPr
4.2g, R^1 = Ph, R^2 = TMS, X = CE_2	**4.2h**, R^1 = Ph, R^2 = $CH{=}CMe_2$, X = CE_2	**4.2i**, $R^1 = R^2$ = Ph, X = benzimidazole
 **4.3a**, 98% Yield, >20:1 dr	 **4.3j**, 85% Yield, >20:1 dr	 **4.3k**, 82% Yield, >20:1 dr
 **4.3l**, 65% Yield, >20:1 dr	 **4.3m**, 73% Yield, >20:1 dr	 **4.3n**, 61% Yield[b,c], 1.6:1 dr
 **4.3o**, 67% Yield[c], >20:1 *syn*	 **4.3p**, 84% Yield, >20:1 dr	 **4.3q**, 64% Yield, >20:1 dr

[a]Yields of material isolated by silica gel chromatography. See Supporting Information for further experimental details.
[b]120 °C, [c]24 Hr.



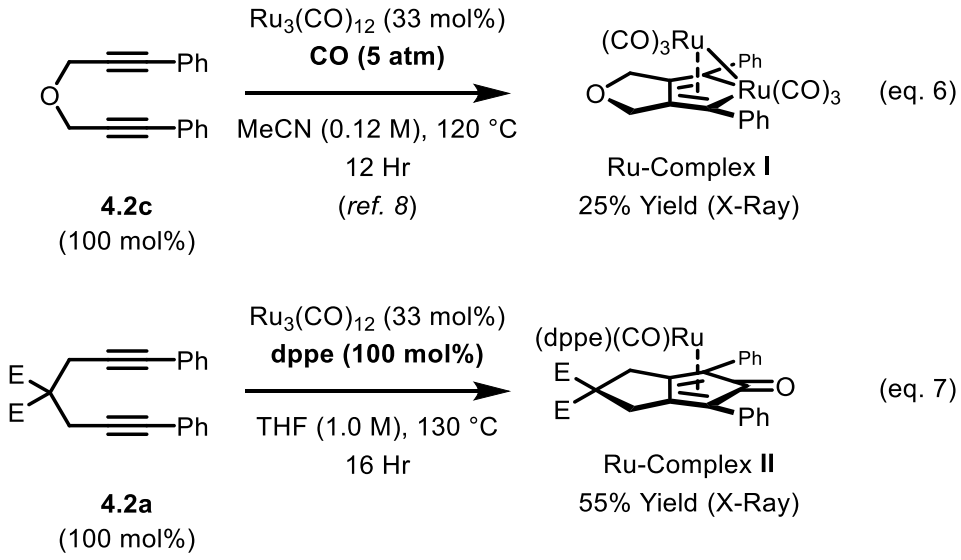
Scheme 4.2. Redox-level independent [2+2+2] cycloaddition of diol **4.1f**, α-ketol dehydro-**4.1f** or vicinal dione didehydro-**4.1f**.[a]

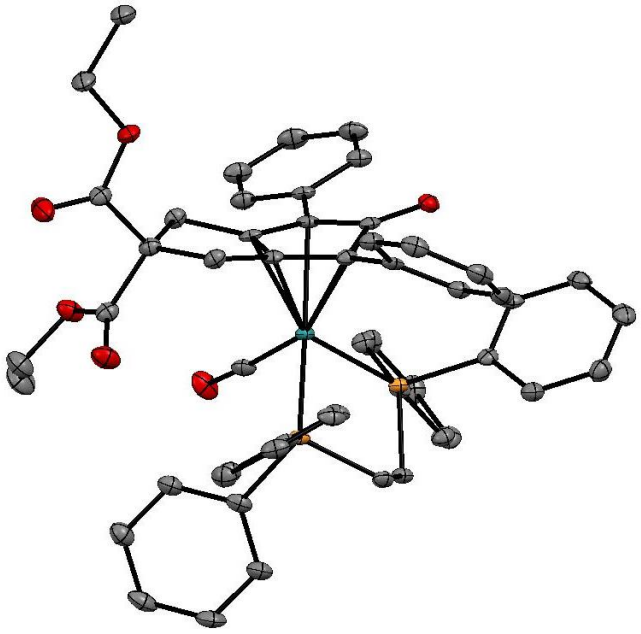
Cycloaddition is postulated to occur between 1,6-diyne and vicinal dione derived from diol and transient α-ketol through dehydrogenation reactions(Figure 4.1). Thus, vicinal diones and α-ketols as well as diols should be effective. While the cycloaddition of diols is an oxidative transformation wherein excess diyne is sacrificed as hydrogen acceptor, the cycloaddition of α-ketols is redox-neutral and the cycloaddition of vicinal diones is a reductive process that requires a hydrogen donor. To demonstrate that the present cycloaddition may be conducted in oxidative, redox-neutral and reductive modes, the reaction of diol **4.1f**, α-ketol *dehydro*-**4.1f** and vicinal dione *didehydro*-**4.1f** were explored (Scheme 4.2). When the same conditions used for cycloaddition of diol **4.1f** (Scheme 4.2, eq. 3) were applied to α-ketol *dehydro*-**4.1f** (Scheme 4.2, eq. 4), each led to the formation of cycloadduct **4.3f** in 80% yield. Reductive cycloaddition of vicinal dione

didehydro-**4.1f** to form **4.3f** also was possible using 2-propanol as a source of hydrogen (Scheme 4.2, eq. 5). Recently, a variety of oxidative[5a,8] and reductive[5a,9] cycloaddition reactions have been reported that provide access to cyclic compounds from unconventional substrates. To our best knowledge, the conversion of dione *didehydro*-**4.1f** to **4.3f** represents the first example of a reductive [2+2+2] cycloaddition reaction.[1]

4.3 Mechanism

The proposed general catalytic mechanism (Figure 4.1) is examined by the following data. As reported by Yamamoto,[10] the dinuclear ruthenacyclopentadiene complex, Ru-Complex **I**, was obtained in the reaction of stoichiometric 1,6-diyne **4.2c** with $Ru_3(CO)_{12}$ under carbon monoxide pressure (Scheme 4.3, eq. 6). It is reported that exposure of $Ru_3(CO)_{12}$ to dppe in benzene solvent and heating provides the mononuclear $Ru(CO)_3$(dppe) complex.[11] Consistent with these two observations, stoichiometric reaction of 1,6-diyne **4.2a** with $Ru_3(CO)_{12}$ and dppe provides the mononuclear ruthenium cyclopentadienone complex, Ru-Complex **II** (Scheme 4.3, eq. 7).[12] Based on those reports and experimental observation, oxidative cyclometallation between mononuclear ruthenium-phosphine complex and 1,6-diyne may be a key feature of the catalytic mechanism.[13] Subsequent carbonyl insertion is supported by the reported similar reaction with rhodium wherein the addition of metalacyclopentadienes to π-electrophiles aldehydes and imines occurs.[6] Finally, carboxylic acid co-catalyzed transfer hydrogenolysis of oxo-ruthenacycles intermediates, the final stage of the catalytic mechanism, has been established in our prior work.[5b]





Scheme 4.3. Stoichiometric reaction of diynes **4.2c** and **4.2a** with $Ru_3(CO)_{12}$ to form Ru-Complex I and Ru-Complex II. Structure of Ru-Complex II as determined by single crystal X-ray diffraction (H-atoms omitted for clarity).[a]

[a]Yields of material isolated by silica gel chromatography (eq. 6) or precipitation (eq. 7). Displacement ellipsoids are scaled to the 50% probability level. See Supporting Information for crystallographic data and further experimental details.

4.4 Summary

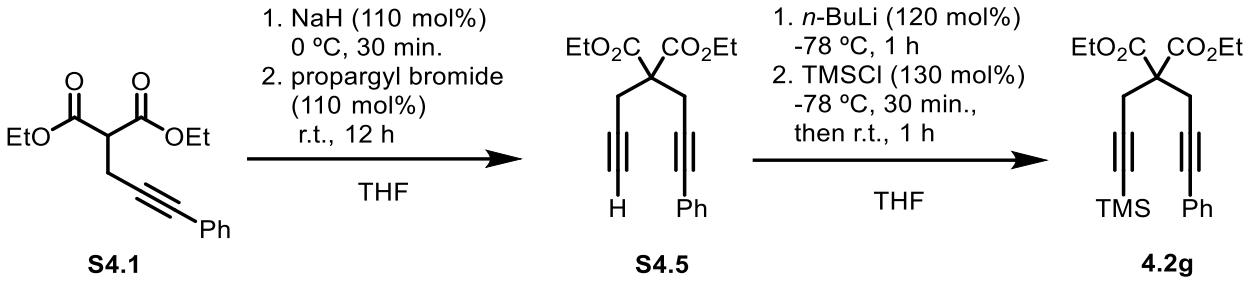
In summary, adding a broad, new dimension to a longstanding cycloadditions chemistry,[14] we achieved the first examples of vicinal diols, ketols or diones as $2_{2\pi}$ components in metal catalyzed [2+2+2] cycloaddition. These processes proceed via ruthenium(0)-mediated oxidative coupling of a 1,6-diyne followed by successive carbonyl addition between the resulting ruthenacyclopentadiene and a transient dione derived from diol. Transfer hydrogenolysis of the resulting ruthenium(II) diolate releases the cycloadduct, and regenerates zero-valent ruthenium.

4.5 Experimental Details

All glassware was oven dried at 120 °C overnight and cooled in a desiccator. All ruthenium catalyzed reactions were carried in sealed pressure tubes (13 x 100 mm). THF was purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], dppe, PCy_3 and 1-adamantane carboxylic acid were purchased from commercial suppliers and used as received. Diols **4.1a**, **4.1b**, **4.1h**, dehydro-**4.1f**, and didehydro-**4.1f** were purchased from commercially available sources and used without purification. **4.1c**,[1] **4.1d**,[1] **4.1e**,[2] **4.1f**,[3] **4.1g**,[4] and **4.1i**[1] were prepared according to previous literature. Diynes **4.2a**,[5] **4.2b**,[5] **4.2c**,[6] and **4.2d**[5] were prepared by Sonogashira reactions following literature procedures. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with a Varian Gemini spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on a Karatos MS9 and are reported as m/z. Masses are reported for the molecular ion (M-H, M, M+H or M+Na).

Synthesis of Starting Materials

Diethyl 2-(but-2-yn-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (4.2e)



Mono-alkyne **S4.1** was synthesized according to known procedures and their characterization data match our own in all respects.

To a solution of alkyne **S4.1** (2.74 g, 10.0 mmol, 110 mol%) in anhydrous THF (25 mL) cooled to 0 °C was added NaH (60% in mineral oil, 440 mg, 11.0 mmol, 110 mol%) portionwise. The mixture was allowed to stir at the same temperature for 30 min followed by the addition of 1-bromo-2-butyne (0.96 mL, 11 mmol, 110 mol%). The reaction was then warmed to room temperature and allowed to stir for 12 hours. The reaction was diluted with EtOAc (25 mL) and washed with water (50 mL). The aqueous layer was then extracted with EtOAc (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 95:5) to furnish the title compound **4.2e** (2.64 g, 8.1 mmol) in 81% yield as a light yellow oil.

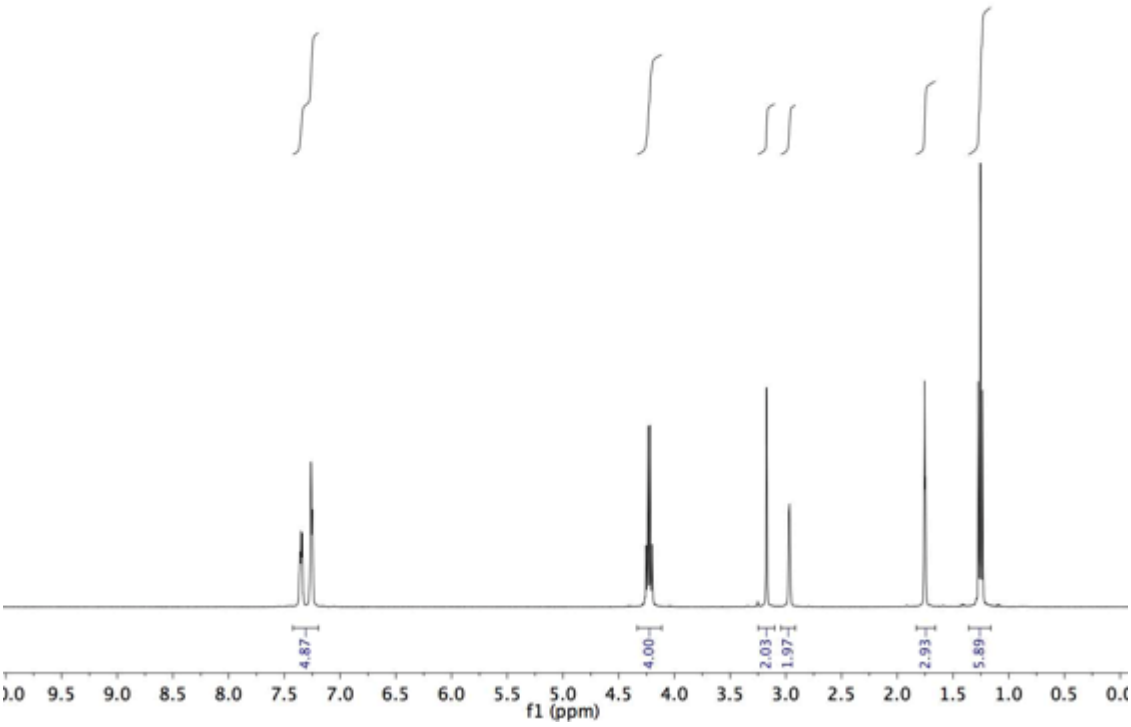
TLC (SiO_2): R_f = 0.24 (hexanes : ethyl acetate = 95:5).

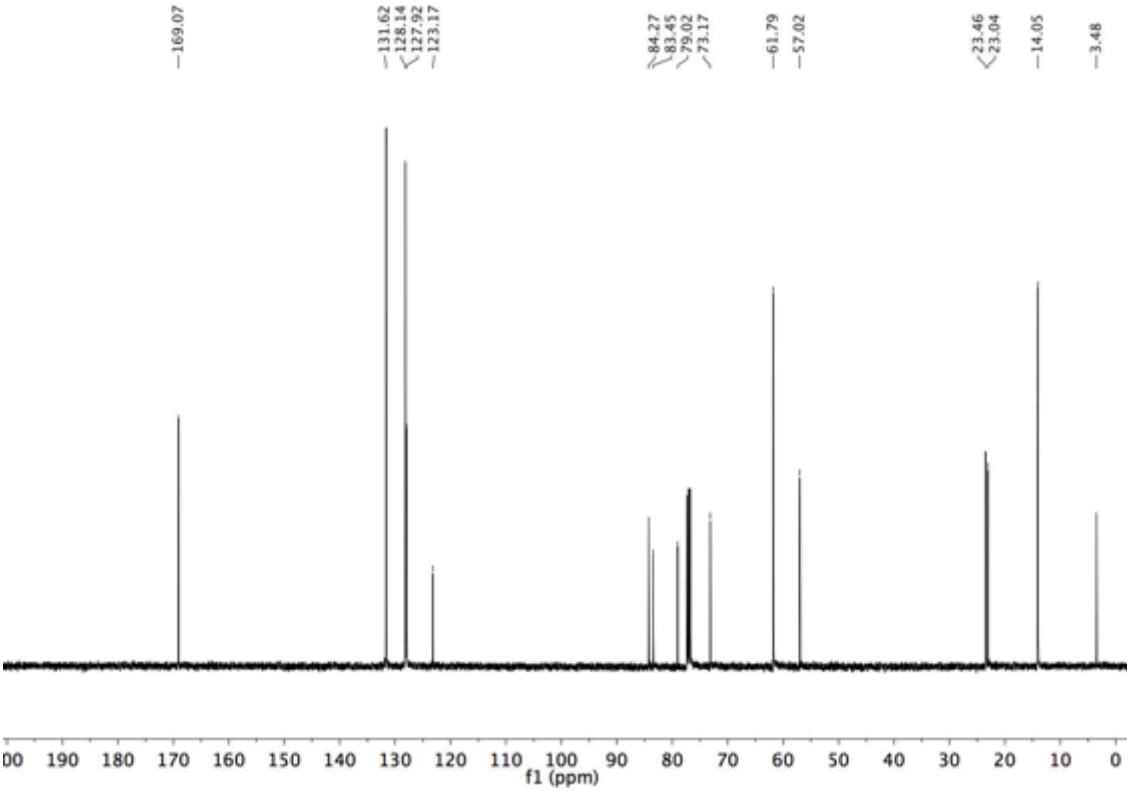
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 5H), 4.24 (q, *J* = 6.7 Hz, 4H), 3.17 (s, 2H), 2.98-2.95 (m, 2H), 1.76-1.74 (m, 3H), 1.28 (t, *J* = 7.8 Hz, 6H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 169.1, 131.6, 128.1, 127.9, 123.2, 84.3, 83.5, 79.0, 73.2, 61.8, 57.0, 23.5, 23.0, 14.1, 3.5 ppm.

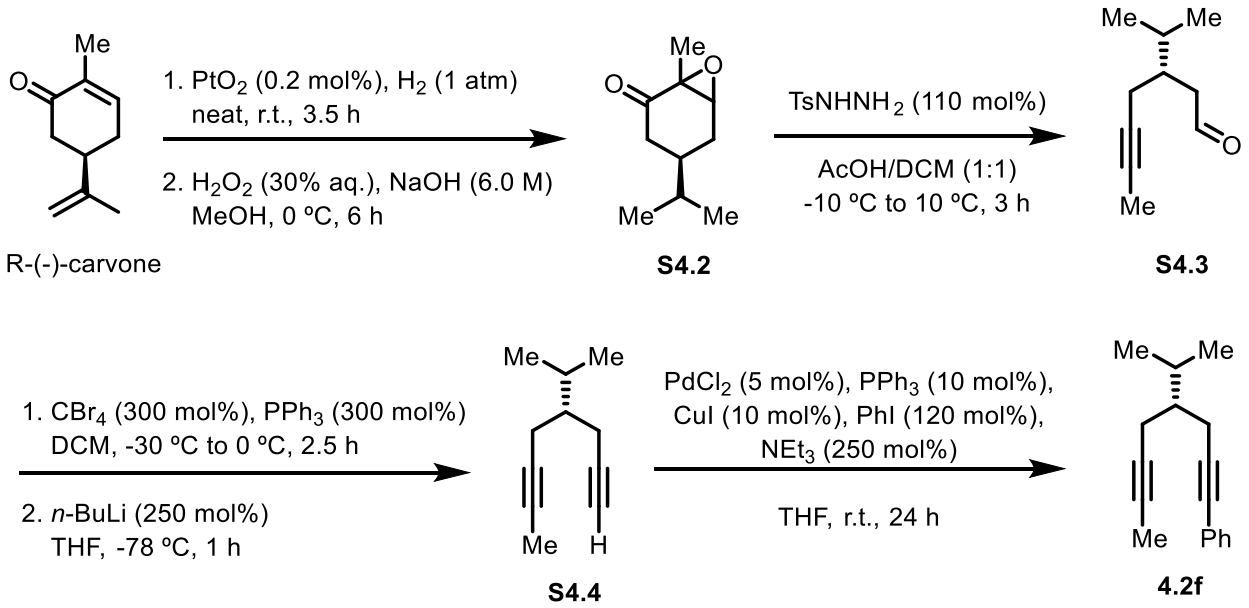
HRMS: (ESI) Calculated for $C_{20}H_{22}O_4$ $[M+Na^+]$ =349.14100, Found 349.14180.

FTIR: (neat): 2977, 2920, 1735 cm^{-1}.


4.87
4.00
2.03
1.97
2.93
5.89
f1 (ppm)


169.07
131.62
128.14
127.92
123.17
84.27
83.45
79.02
73.17
61.79
57.02
23.46
23.04
14.05
3.48
f1 (ppm)

(*S*)-(4-isopropylocta-1,6-diyn-1-yl)benzene (4.2f)



Epoxy ketone **S4.2** was synthesized according to literature procedures and the characterization is identical in all respects.

Synthesis of aldehyde **S4.3** from epoxy ketone **S4.2**:

Aldehyde **S4.3** was prepared according to a literature procedure.[15] To a solution of epoxy ketone **S4.2** (5.66g, 33.6 mmol, 100 mol%) in mixture of DCM and acetic acid (94 mL, 1:1) at -10 °C was added *p*-toluenesulfonyl hydrazide (6.89g, 37.0 mmol, 110 mol%) portionwise. The reaction was warmed to 10 °C slowly over 3 hours. The reaction was then washed with ice-cold water (200 mL). The aqueous layer was then extracted with DCM (3 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2;

hexanes: Et_2O = 95:5) to furnish the title compound **S4.3** (2.14 g, 14.1 mmol) in 42% yield as a colorless oil.

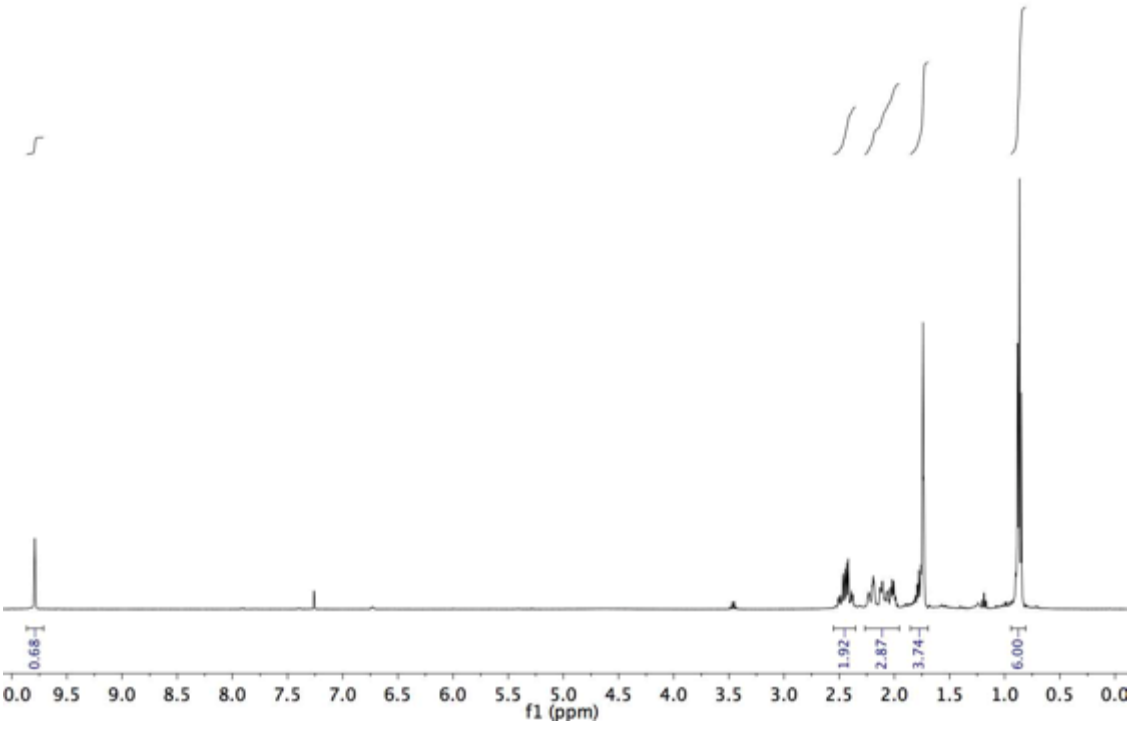
TLC (SiO_2): R_f = 0.53 (hexanes : Et_2O = 95:5).

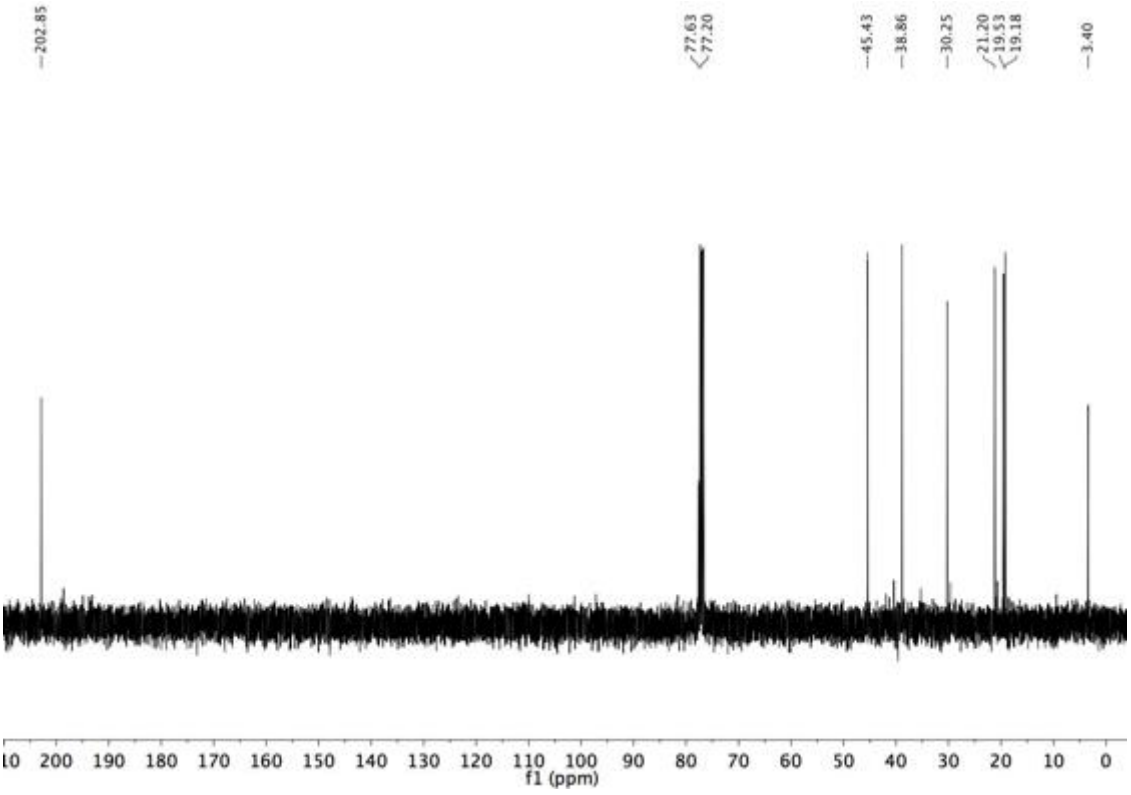
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 2.52-2.38 (m, 2H), 2.27-1.99 (m, 3H), 1.76-1.72 (m, 4H), 0.87 (t, *J* = 6.7 Hz, 6H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 202.9, 77.6, 77.2, 45.4, 38.9, 32.3, 21.2, 19.5, 19.2, 3.4 ppm.

HRMS: (CI^+) Calculated for $C_{10}H_{15}O$ [M-H^+] =151.1123, Found151.1118.

FTIR: (neat): 2961, 2917, 2873, 1706 cm^{-1}.


0.68
1.92
2.87
3.74
6.00
f1 (ppm)


202.85
77.63
77.20
45.43
38.86
30.25
21.20
19.53
19.18
3.40
f1 (ppm)

Synthesis of diyne **S4.4** from aldehyde **S4.3**:

Diyne **S4.4** was prepared according to literature procedure.[16] To a solution of carbon tetrabromide (13.8 g, 41.7 mmol, 300 mol%) in DCM (65 mL) at -30 °C was added a solution of triphenyl phosphine (10.94 g, 41.7 mmol, 300 mol%) in DCM (15 mL). The mixture was allowed to stir at the same temperature for 30 minutes. A solution of aldehyde **S4.3** (2.12 g, 13.9 mmol, 100 mol%) in DCM (10 mL) was then added. The reaction was warmed to 0 ˚C and allowed to stir for 2 hours. The mixture was then filtered through a short pad of celite and washed with DCM (6 x 10 mL). The filtrate was then washed successively with water (100 mL) and brine (100 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to filtration over silica gel with hexanes.

To a solution of the product in anhydrous THF (110 mL) at -78 °C under an Ar-atmosphere was added *n*-BuLi (2.5 M solution of hexanes, 13.9 mL, 34.8 mmol, 250 mol% to **S4.3**) dropwise. The reaction was allowed to stir at the same temperature for 1 hour, and then was quenched with saturated NH_4Cl solution. The mixture was concentrated and then washed with water (100 mL). The aqueous layer was then extracted with hexanes (3 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to filtration over silica gel with hexanes to furnish **S4.4** as a yellow oil, which was subjected to the following step without further purification.

Synthesis of diyne **4.2f** from diyne **S4.4**:

To an oven-dried flask were added $PdCl_2$ (86.0 mg, 0.48 mmol, 5 mol%), PPh_3 (254 mg, 0.97 mmol, 10 mol%) and CuI (185 mg, 0.97 mmol, 10 mol%), and the flask was purged with Ar three times. Anhydrous THF (15 mL), triethylamine (3.4 mL, 24.2 mmol, 250 mol%), and iodobenzene

(1.3 mL, 11.6 mmol, 120 mol%) were subsequently added and the mixture was allowed to stir at room temperature for 10 minutes. A solution of diyne **S4.4** (1.44 g, 9.69 mmol, 100 mol%) in anhydrous THF (5 mL) was then added. The reaction was allowed to stir at room temperature for 24 hours. The mixture was then filtered through a short pad of celite and washed with EtOAc (6 x 15 mL). The solvent was removed under reduced pressure and the residue was subjected to flash column chromatography (SiO_2; hexanes = 100) to furnish diyne **4.2f** (828.8 mg, 3.69 mmol) in 27% yield over 3 steps from **S4.3** to **4.2f** as a yellow oil.

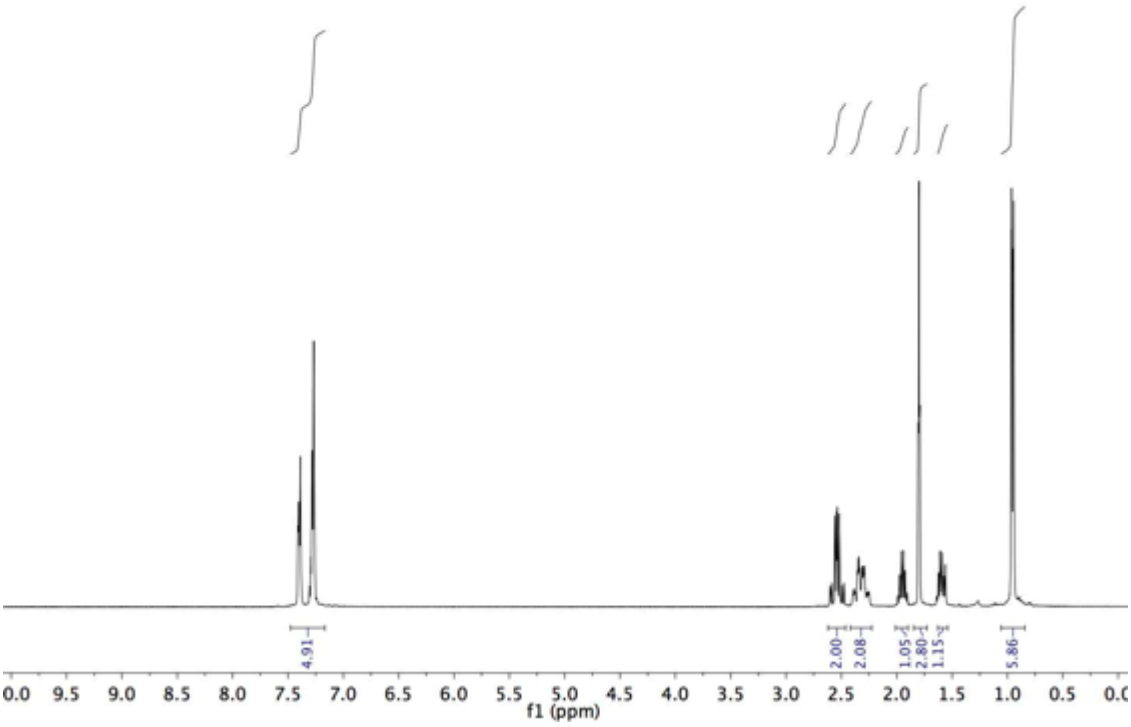
TLC (SiO_2): R_f = 0.35 (hexanes = 100).

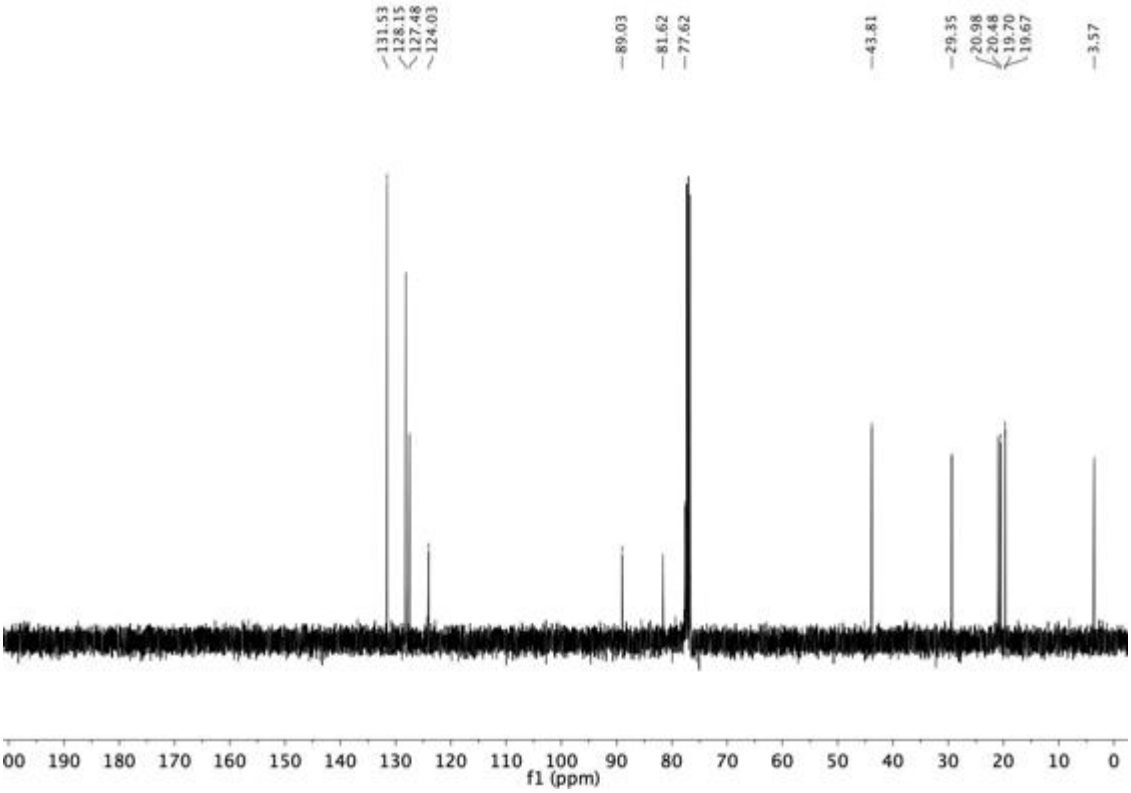
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.41-7.20 (m, 5H), 2.62-2.47 (m, 2H), 2.42-2.24 (m, 2H), 1.96 (q, *J* = 7.0 Hz, 1H), 1.80 (s, 3H), 1,64-1.56 (m, 1H), 0.95 (d, *J* = 6.0 Hz, 6H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 131.5, 128.2, 127.5, 124.0, 89.0, 81.6, 77.6, 43.8, 29.4, 21.0, 20.5, 19.7, 19.7, 3.6 ppm.

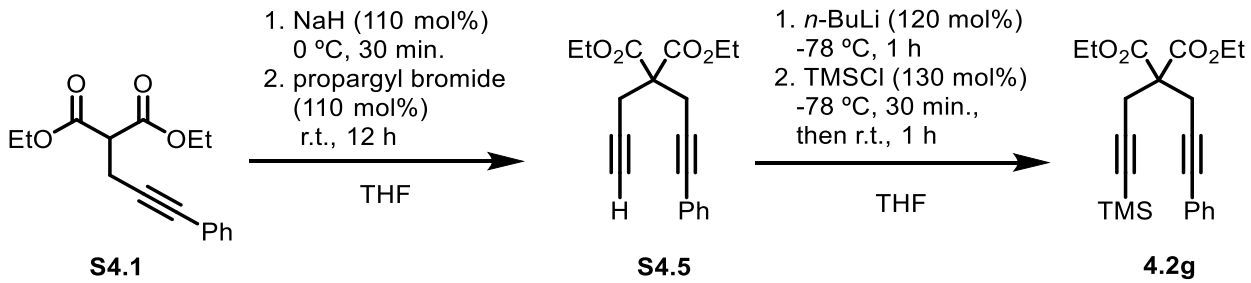
HRMS: (Cl^+) Calculated for $C_{17}H_{19}$ [M^+] =224.1565, Found 224.1562.

FTIR: (neat): 3455, 3016, 2970, 2948, 1736, 1366, 1228 cm^{-1}.


4.91
2.00
2.08
1.05
2.80
1.15
5.86
f1 (ppm)


131.53
128.15
127.48
124.03
89.03
81.62
77.62
43.81
29.35
20.98
20.48
19.70
19.67
3.57
f1 (ppm)

Diethyl 2-(3-phenylprop-2-yn-1-yl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)malonate (**4.2g**)



Synthesis of diyne **S4.5** from **S4.1**:

A solution of alkyne **S4.1** (5.49 g, 20.0 mmol, 100 mol%) in anhydrous THF (50 mL) cooled to 0 °C. NaH (60% in mineral oil, 880 mg, 22.0 mmol, 110 mol%) was then added portionwise. The mixture was allowed to stir at the same temperature for 30 min, followed by the addition of propargyl bromide (80% w/w solution in toluene, 2.45 mL, 22.0 mmol, 110 mol%). The reaction was allowed to warm to room temperature over 12 hours. The reaction was diluted with EtOAc (50 mL) and washed with water (100 mL). The aqueous layer was then extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine (60 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes: Et_2O = 95:5) to furnish the title compound **S4.5** (5.06 g, 16.2 mmol) in 81% yield as a yellow oil.

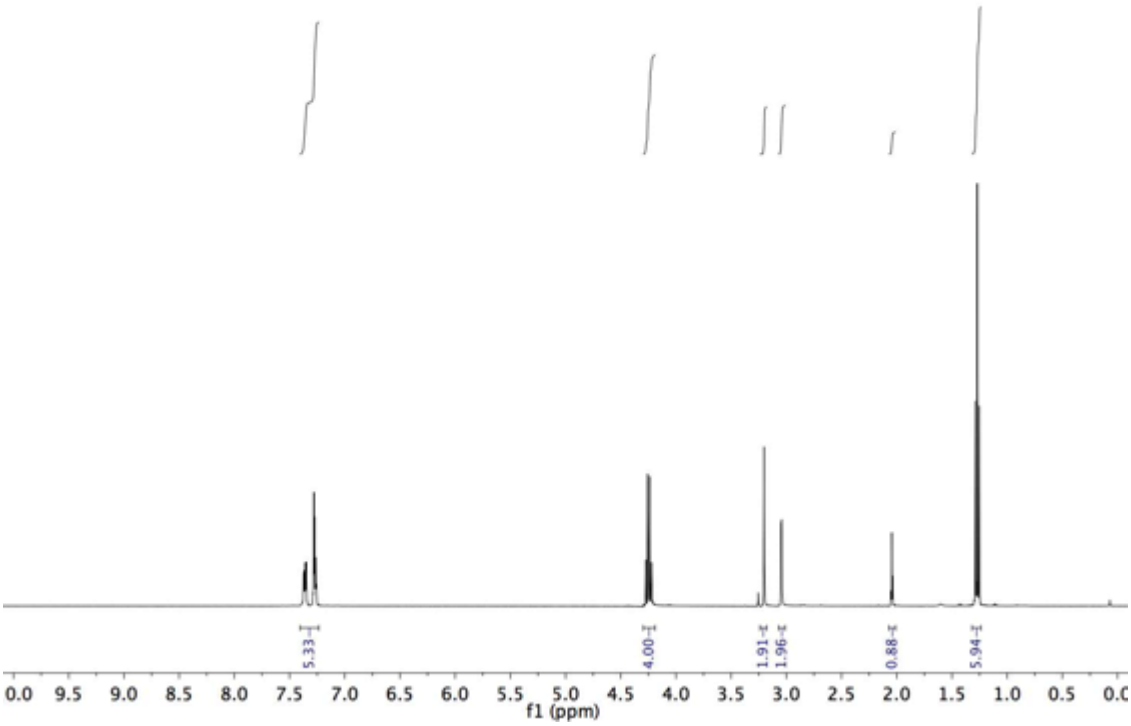
TLC (SiO_2): R_f = 0.24 (hexanes : ethyl acetate = 95:5).

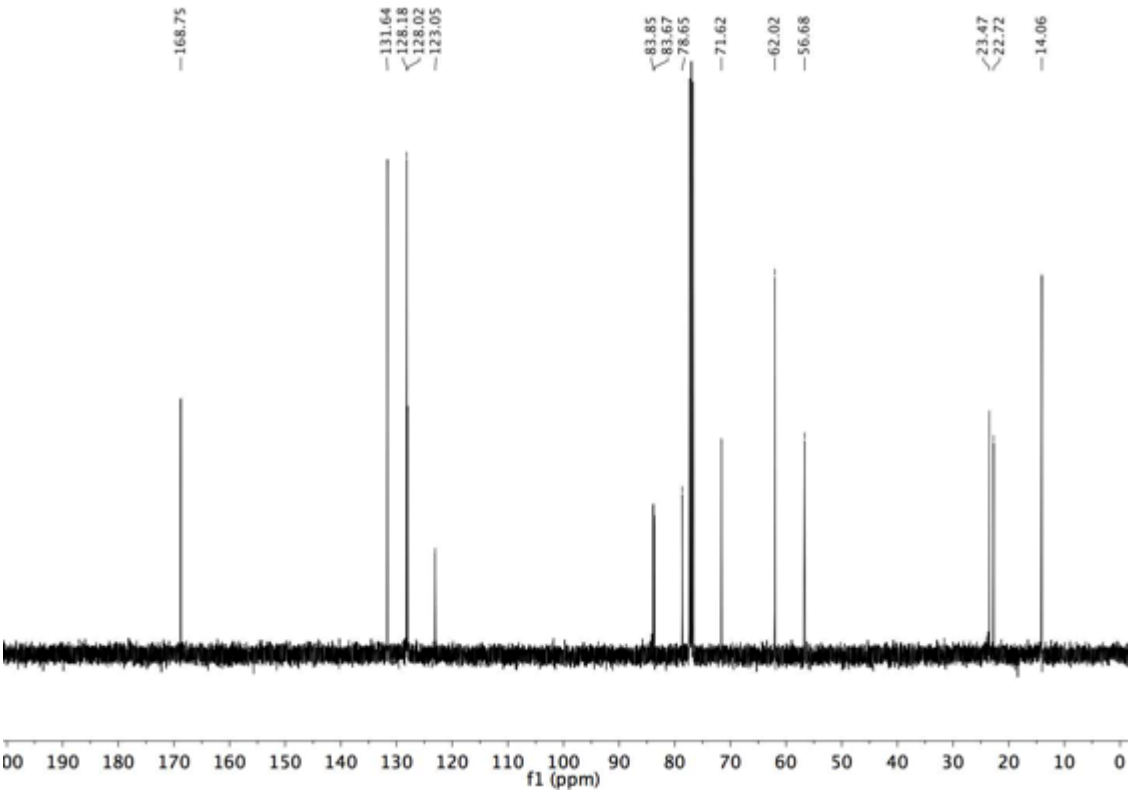
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.38-7.24 (m, 5H), 4.25 (q, *J* = 7.3 Hz, 4H), 3.20 (s, 2H), 3.04 (d, *J* = 2.7 Hz, 2H), 2.04 (t, *J* = 2.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 168.8, 131.6, 128.2, 128.0, 123.1, 83.9, 83.7, 78.7, 71.6, 62.0, 56.7, 23.5, 22.7, 14.1 ppm.

HRMS: (ESI) Calculated for $C_{19}H_{20}O_4$ [M+Na^+] =335.12540, Found335.1266.

FTIR: (neat):2911, 2983, 1735 cm^{-1}.


5.33
4.00
1.91
1.96
0.88
5.94
f1 (ppm)


168.75
131.64
128.18
128.02
123.05
83.85
83.67
78.65
71.62
62.02
56.68
23.47
22.72
14.06
f1 (ppm)

Synthesis of diyne **4.2g** from **S4.5**:

A solution of diyne **S4.5** (1.87 g, 6.00 mmol, 100 mol%) in anhydrous THF (12 mL) was cooled to -78 °C under an Ar-atmosphere. *n*-BuLi (2.5 M solution in hexanes, 2.88 mL, 7.2 mmol, 120 mol%) was then added dorpwise. The mixture was allowed to stir at the same temperature for 1 hour followed by the addition of TMSCl (0.99 mL, 7.8 mmol, 130 mol%). The reaction was allowed to stir at -78 °C for 30 min, then at room temperature for 1 hour. The reaction was subsequently quenched by the addition of saturated NH_4Cl solution. The reaction was diluted with ether (15 mL) and washed with water (30 mL). The aqueous layer was then extracted with Et_2O (3 x 20 mL) and the combined organic layers were washed with brine (30 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes: ethyl acetate =98:2 to 95:5) to furnish the title compound **4.2g** (1.41 g, 3.66 mmol) in 61% yield as a light yellow oil.

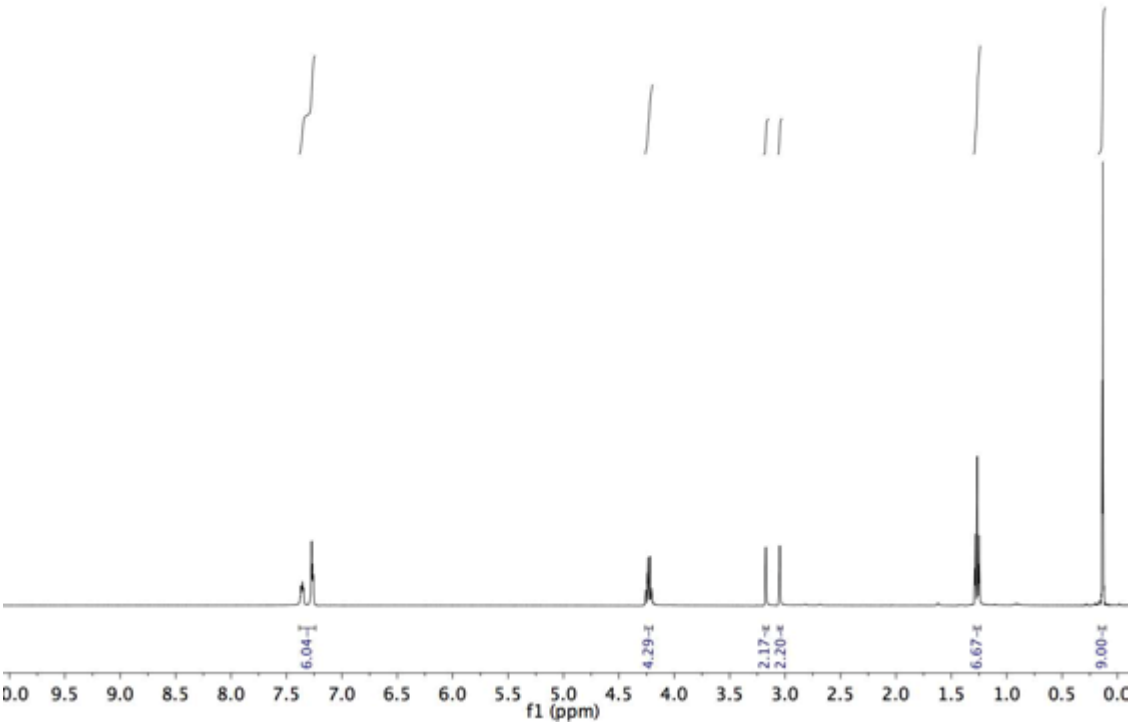
TLC (SiO_2): R_f = 0.26 (hexanes : ethyl acetate = 95:5).

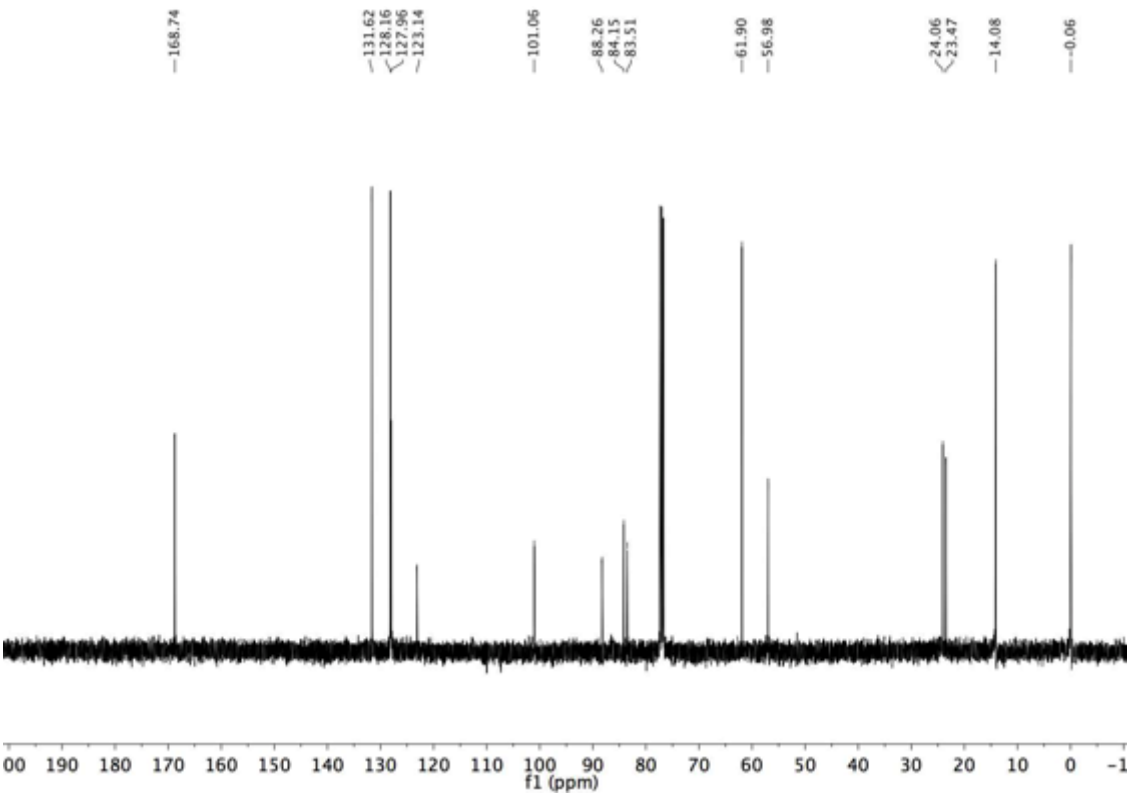
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.37-7.24 (m, 5H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.18 (s, 2H), 3.05 (s, 2H), 1.27 (t, *J* = 7.3 Hz, 6H), 0.14 (s, 9H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 168.7, 131.6, 128.2, 128.0, 123.1, 101.1, 88.3, 84.2, 83.5, 61.9, 57.0, 24.1, 23.5, 14.1, -0.1 ppm.

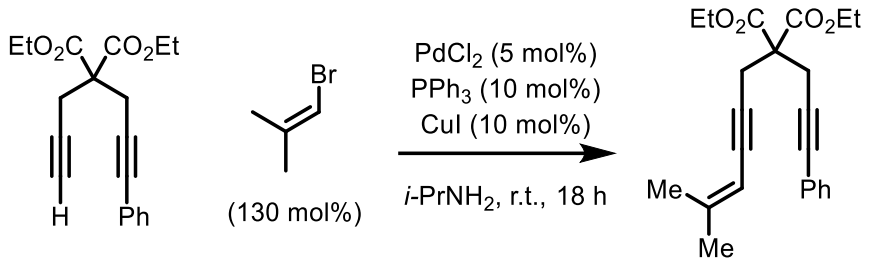
HRMS: (ESI) Calculated for $C_{22}H_{28}O_4Si$ $[M+H^+]$ =385.18300, Found 385.18330.

FTIR: (neat): 2958, 2179, 1737 cm^{-1}.


6.04
4.29
2.17
2.20
6.67
9.00
f1 (ppm)


168.74
131.62
128.16
127.96
123.14
101.06
88.26
84.15
83.51
61.90
56.98
24.06
23.47
14.08
-0.06
f1 (ppm)

Diethyl 2-(5-methylhex-4-en-2-yn-1-yl)-2-(3-phenylprop-2-yn-1-yl)malonate (4.2h)



S4.5 **4.2h**

To an oven-dried flask was added $PdCl_2$ (43.0 mg, 0.24 mmol, 5 mol%), PPh_3 (127.2 mg, 0.49 mmol, 10 mol%) and CuI (92.4 mg, 0.49 mmol, 10 mol%), and the flask was purged with Ar. *i*-$PrNH_2$ (6 mL) was then added and the mixture was allowed to stir at room temperature under an Ar-atmosphere for 5 minutes. 1-Bromo-2-methyl-1-propene (0.65 mL, 6.30 mmol, 130 mol%) and a solution of diyne **S4.5** (1.51 g, 4.85 mmol, 100 mol%) in *i*-$PrNH_2$ (4 mL) were subsequently added and the reaction was allowed to stir at room temperature for 18 hours. The mixture was then filtered through a short pad of celite and washed with EtOAc (6 x 15 mL). To the combined filtrate was added charcoal (5 g), and the mixture was allowed to stir at room temperature for 1 hour. The mixture was then filtered again through a short pad of celite and washed with EtOAc (6 x 15 mL). All volatiles were removed under reduced pressure and the residue was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 97:3 to 95:5) to give diyne **4.2h** (698.4 mg, 1.89 mmol) in 39% yield as a light yellow oil.

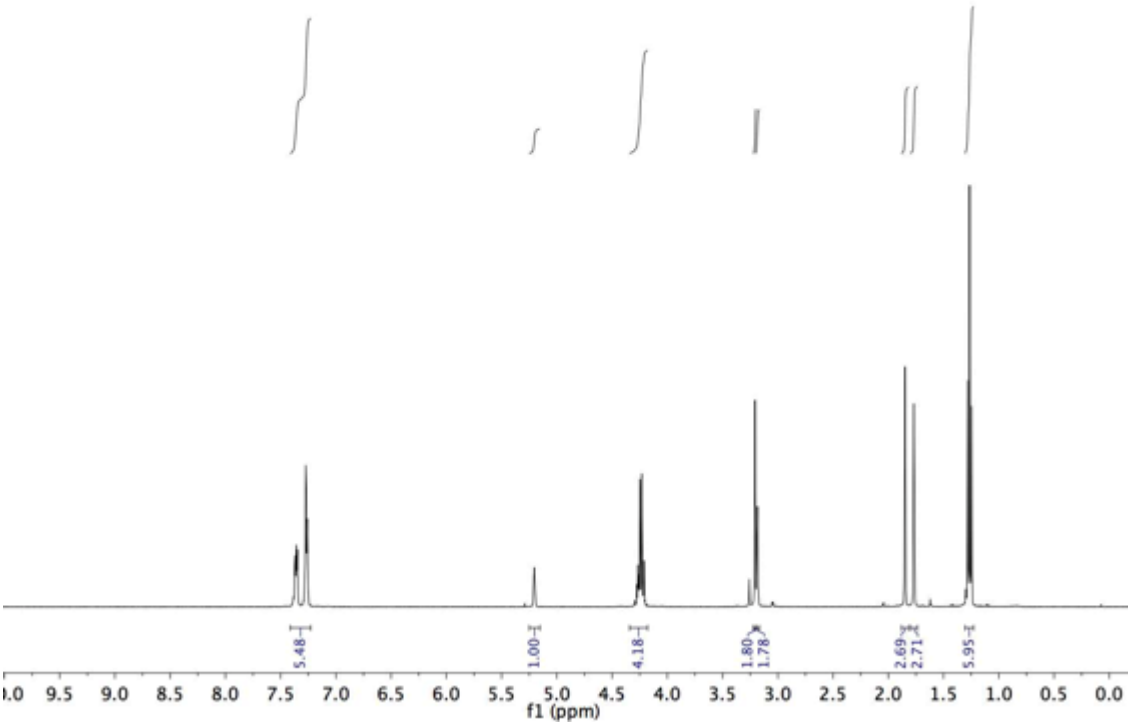
TLC (SiO_2): R_f = 0.24 (hexanes : ethyl acetate = 95:5).

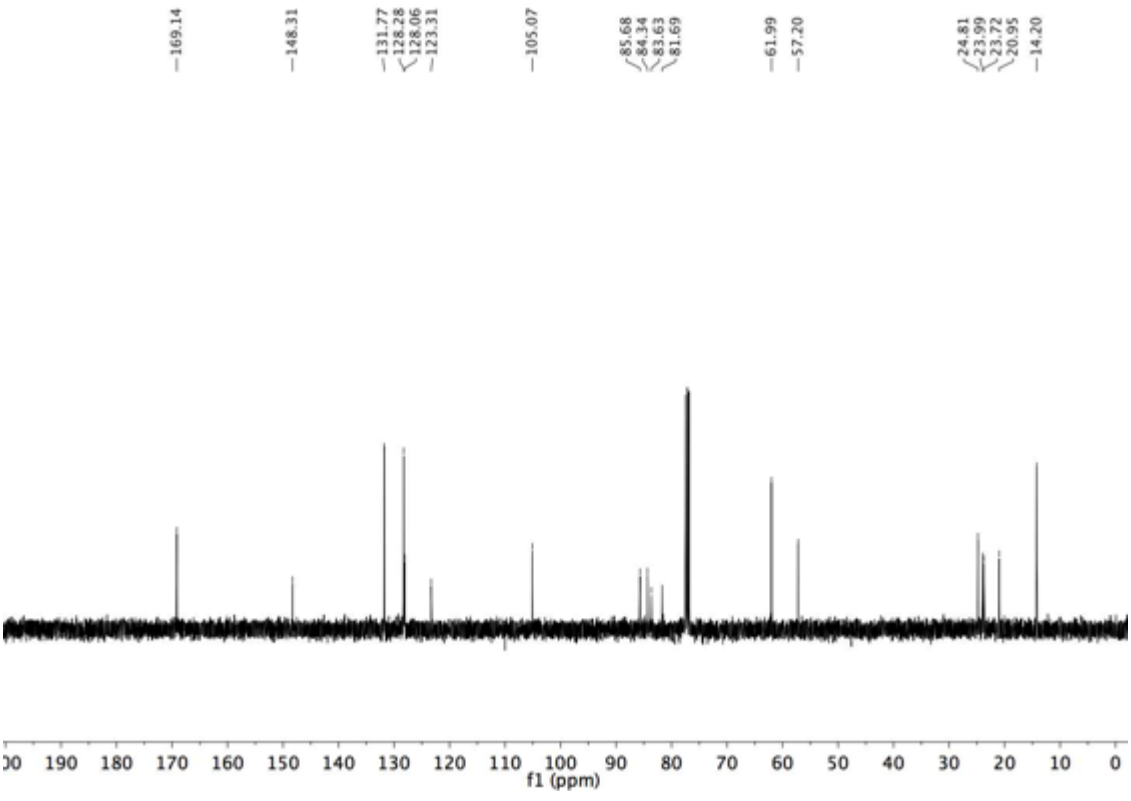
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.41-7.24 (m, 5H), 5.21 (s, 1H), 4.25 (q, *J* = 7.3 Hz, 4H), 3.23 (s, 2H), 3.18 (s, 2H), 1.85 (s, 3H), 1.77 (s, 3H), 1.27 (q, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 169.1, 148.3, 131.8, 128.3, 128.1, 123.3, 105.1, 85.7, 84.3, 83.6, 81.7, 62.0, 57.2, 24.8, 24.0, 23.7, 21.0, 14.2 ppm.

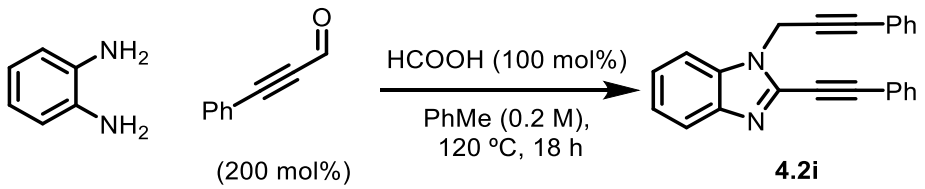
HRMS: (ESI) Calculated for $C_{23}H_{26}O_4$ $[M+H^+]$ =367.19040, Found 367.19130.

FTIR: (neat): 2977, 2904, 1735 cm^{-1}.


5.48
1.00
4.18
1.80
1.78
2.69
2.71
5.95
f1 (ppm)


169.14
148.31
131.77
128.28
128.06
123.31
105.07
85.68
84.34
83.63
81.69
61.99
57.20
24.81
23.99
23.72
20.95
14.20
f1 (ppm)

2-(phenylethynyl)-1-(3-phenylprop-2-yn-1-yl)-1*H*-benzo[*d*]imidazole (4.2i)



Imidazole **4.2i** was prepared according to literature procedure.[16] To an oven-dried flask were added 1,2-benzenediamine (108.1 mg, 3.80 mmol, 100 mol%), Phenylpropargyl aldehyde (1.0 g, 7.7 mmol, 200 mol%) and formic acid (0.14 mL, 3.8 mmol, 100 mol%). PhMe (35 mL) was added and the mixture was heated to 120 ˚C for 18 h using a Dean Stark apparatus. The mixture was then cooled to room temperature and concentrated under reduced pressure. The crude solid was subjected to column chromatography (SiO_2; hexanes:ethyl acetate = 90:10) and then recrystallized (benzene/hexanes) to furnish the title compound **4.2i** (556 mg, 1.7 mmol) in 44% yield as a white solid.

TLC (SiO_2): R_f = 0.80 (hexanes : ethyl acetate = 1:1).

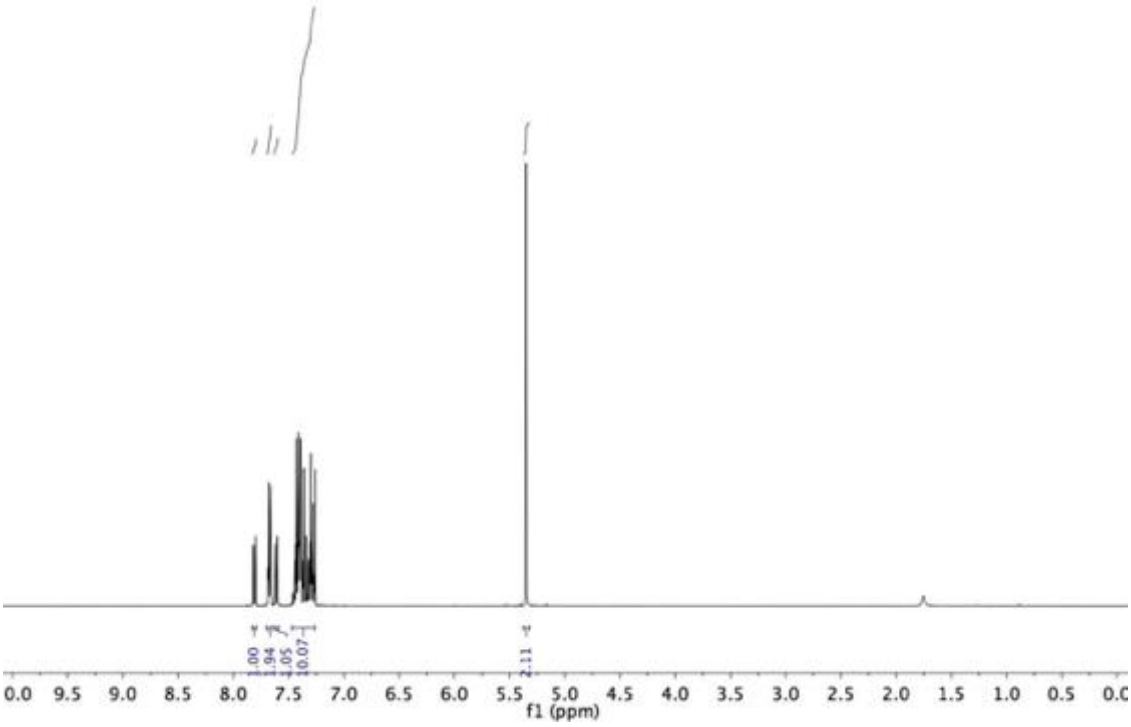
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.82-7.80 (m, 1H), 7.69-7.66 (m, 2H), 7.62-7.60 (m, 1H), 7.43-7.26 (m, 10H), 5.35 (s, 2H) ppm.

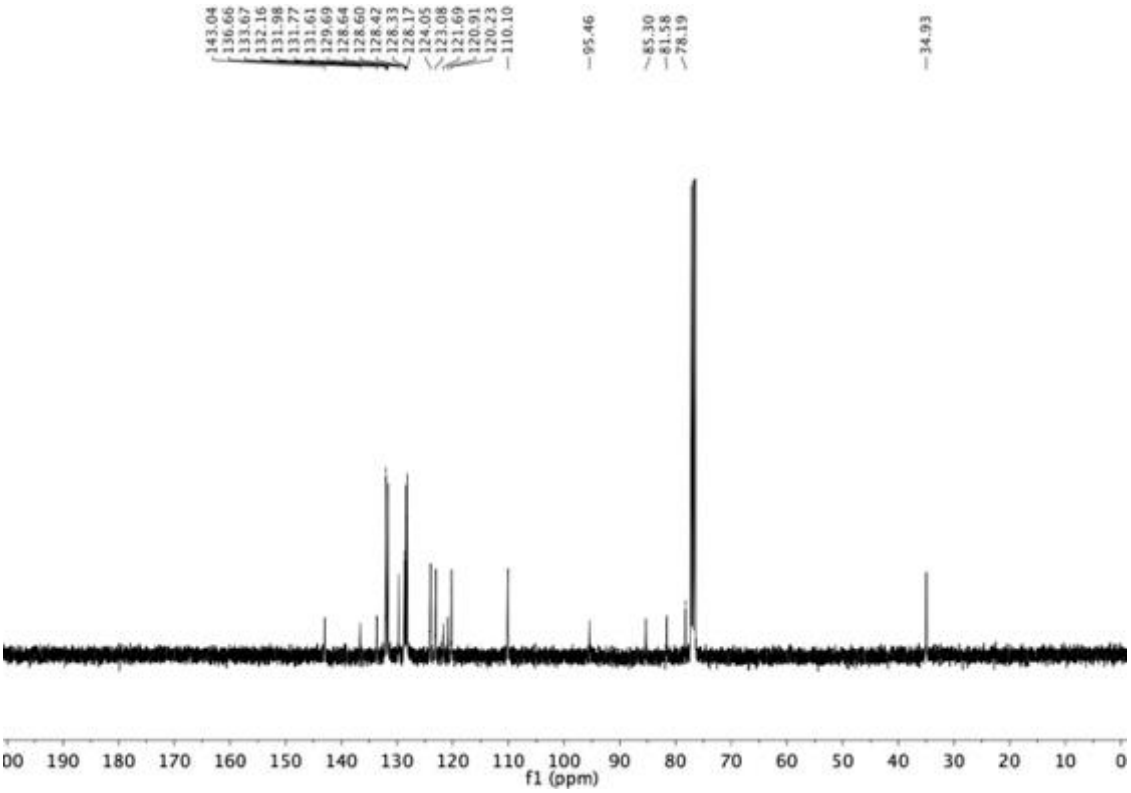
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 143.0, 136.7, 136.7, 132.2, 132.0, 131.8, 131.6, 129.7, 128.6, 128.6, 128.4, 128.3, 128.2, 124.1, 123.1, 121.7, 120.9, 120.2, 110.1, 95.5, 85.3, 81.6, 78.2, 34.9 ppm.

MP: 157 - 161 °C.

HRMS: (ESI) Calculated for $C_{24}H_{16}N_2$ [M+H$^+$] = 333.13860, Found 333.13980.

FTIR: (neat): 1450, 1356, 746, 687 cm^{-1}.

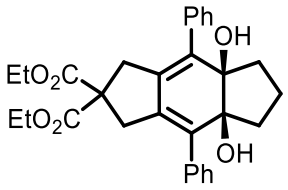

1.00
1.94
1.05
10.07
2.11
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.04
136.66
133.67
132.16
131.98
131.77
131.61
129.69
128.64
128.60
128.42
128.33
128.17
124.05
123.08
121.69
120.91
120.23
110.10
95.46
85.30
81.58
78.19
34.93
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

General Procedure and Spectral Data for Cycloaddition Reaction

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), AdCO_2H (3.2 mg, 0.018 mmol, 6 mol%), diol (0.3 mmol, 100 mol%) and diyne (0.6 mmol, 200 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.5 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 14 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **4.3a-4.3f**.

Diethyl (4a*R*,7a*S*)-4a,7a-dihydroxy-4,8-diphenyl-3,4a,5,6,7,7a-hexahydro-*s*-indacene-2,2(1*H*)-dicarboxylate (4.3a)



The reaction was conducted with *cis*-cyclopentane-1,2-diol **4.1a** in accordance with the general procedure. Flash column chromatography (SiO_2, Et_2O:DCM = 1.5:98.5 to 3:97 with 0.1% NEt_3) provided the title compound **4.3a** (143.6 mg, 0.29 mmol) in 98% yield as a white solid.

TLC (SiO_2): R_f = 0.40 (hexanes : ethyl acetate = 2:1).

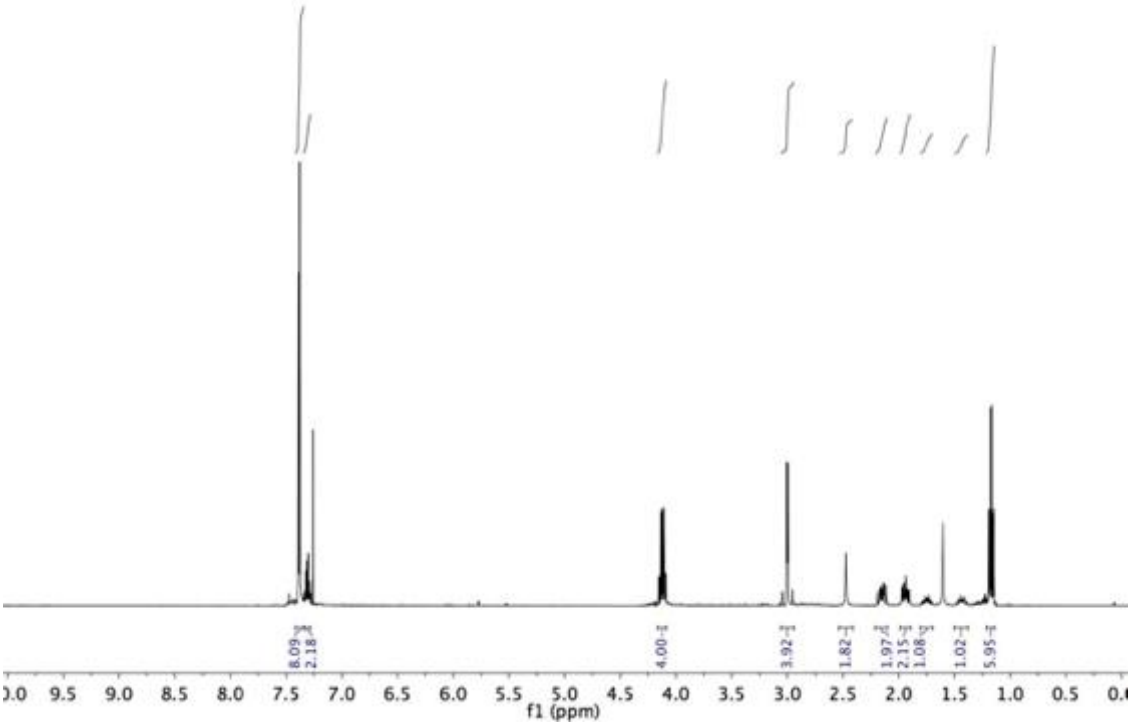
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.39-7.33 (m, 8H), 7.32-7.28 (m, 2H), 4.16-4.09 (m, 4H), 3.03 (d, *J* = 17.1 Hz, 2H), 3.00-2.95 (d, *J* = 17.1 Hz, 2H), 2.48 (s, 2H), 2.19-2.11 (m, 2H), 1.97-1.90 (m, 2H), 1.76-1.72 (m, 1H), 1.22-1.40-1.49 (m, 1H), 1.71-1.78 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm.

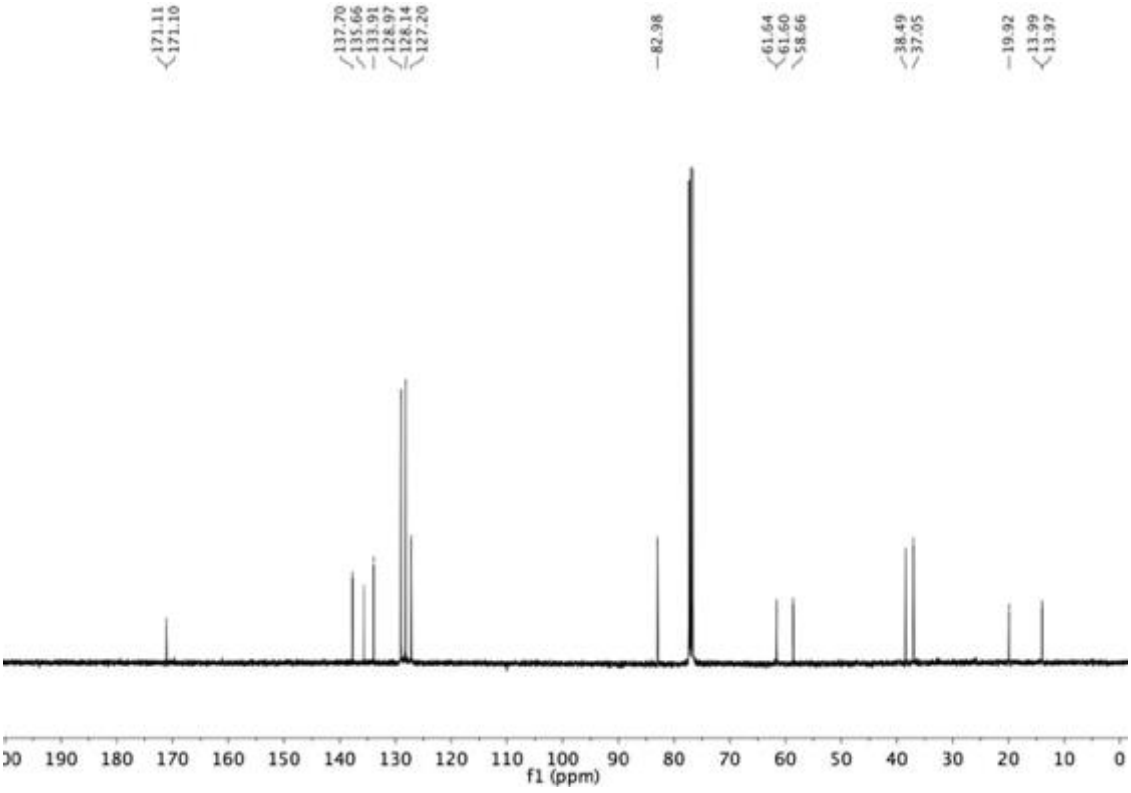
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.1, 171.1, 137.7, 135.7, 133.9, 129.0, 128.1, 127.2, 83.0, 61.6, 61.6, 58.7, 38.5, 37.1, 19.9, 14.0, 14.0 ppm.

MP: 150 - 154 °C.

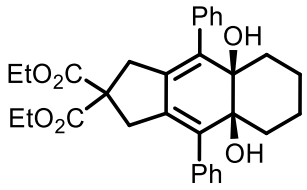
HRMS: (ESI) Calculated for $C_{30}H_{32}O_6$ [M+Na^+] = 511.20910, Found 511.20960.

FTIR: (neat): 3479, 2976, 1729 cm^{-1}.


8.09
2.18
4.00
3.92
1.82
1.97
2.15
1.08
1.02
5.95
f1 (ppm)


171.11
171.10
137.70
135.66
133.91
128.97
128.14
127.20
82.98
61.64
61.60
58.66
38.49
37.05
19.92
13.99
13.97
f1 (ppm)

Diethyl (4a*R*,8a*S*)-4a,8a-dihydroxy-4,9-diphenyl-1,3,4a,5,6,7,8,8a-octahydro-2*H*-cyclopenta[*b*] naphthalene-2,2-dicarboxylate (**4.3b**)



The reaction was conducted with *trans*-cyclohexane-1,2-diol **4.1b** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethylacetate = 75:25) provided the title compound **4.3b** (138.7 mg, 0.28 mmol) in 92% yield as a pale yellow solid.

TLC (SiO_2): R_f = 0.30 (hexanes : ethyl acetate = 3:1).

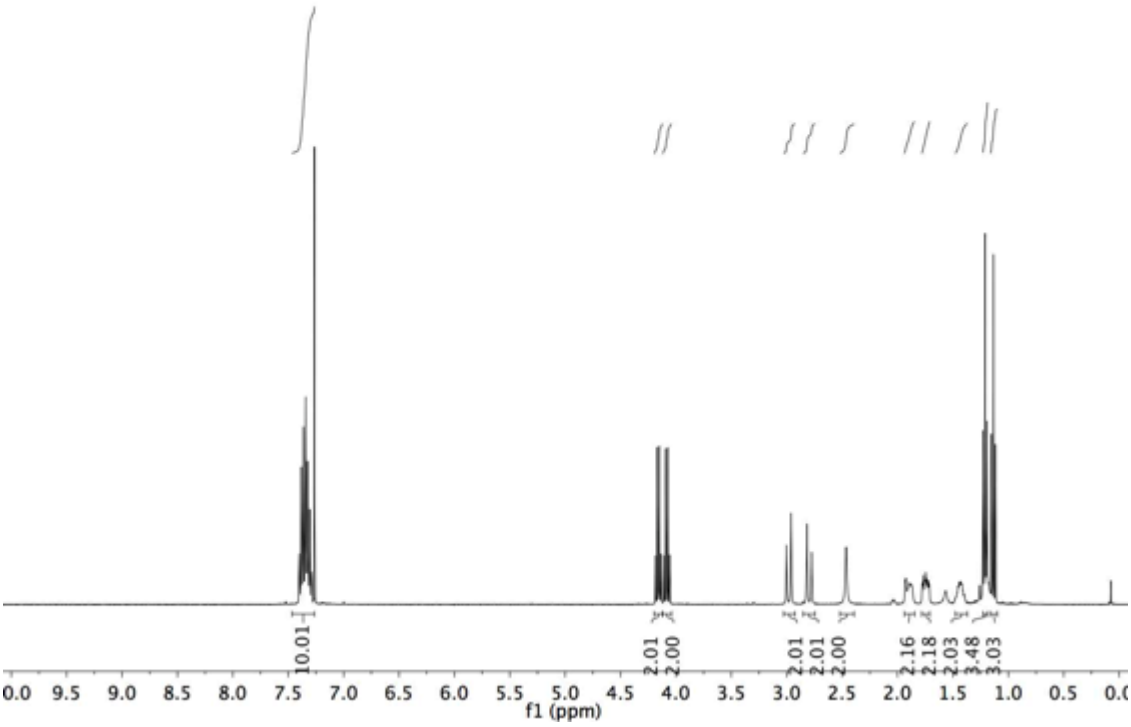
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.40-7.28 (m, 10H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.98 (d, *J* = 16.7 Hz, 2H), 2.80 (d, *J* = 16.7 Hz, 2H), 2.46 (brs, 2H), 1.94-1.86 (m, 2H), 1.78-1.71 (m, 2H), 1.49-1.40 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.26-1.18 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H) ppm.

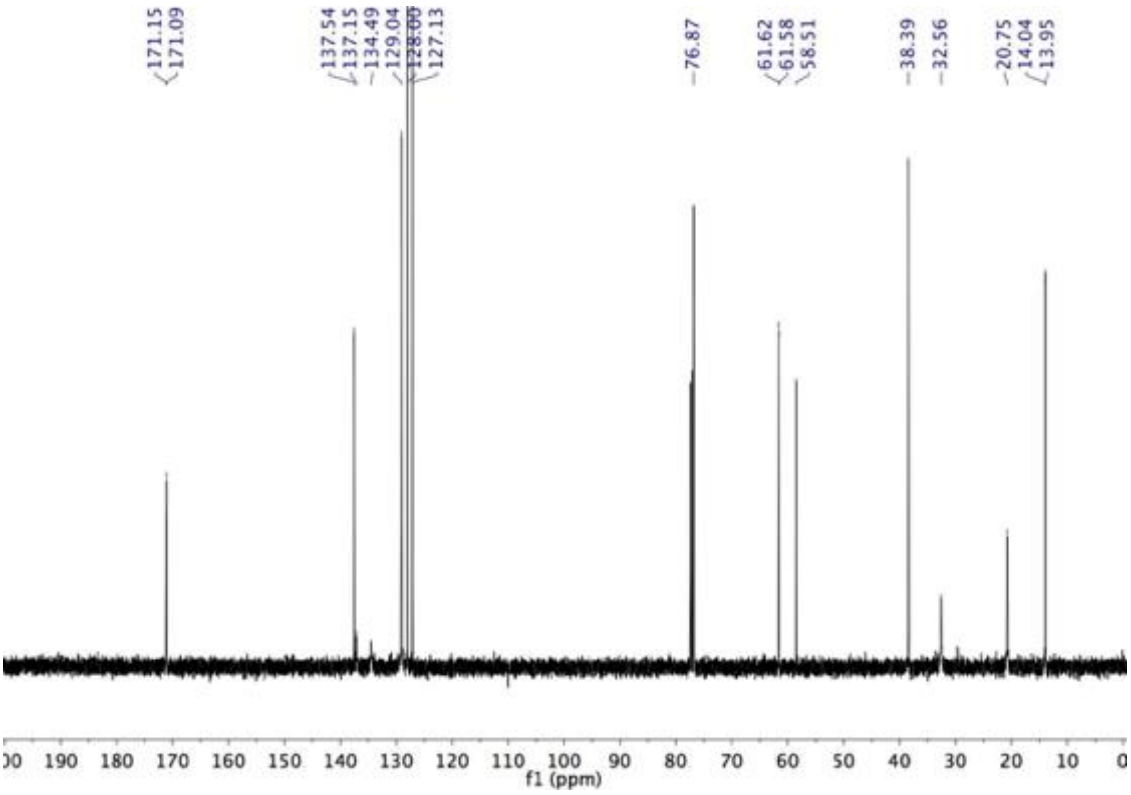
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.2, 171.1, 137.5, 134.5, 129.0, 128.0, 127.1, 76.8, 61.6, 61.6, 58.5, 38.4, 32.6, 20.8, 14.0, 14.0 ppm.

MP: 77 – 78 ˚C.

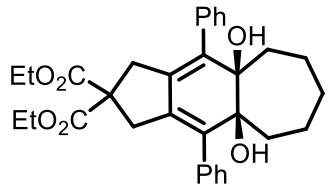
HRMS: (ESI) Calculated for $C_{31}H_{34}O_6$ [M+Na^+] =525.22510, Found 525.22480.

FTIR: (neat): 3438, 3335, 3051, 2982, 2920, 1716 cm^{-1}.


10.01
2.01
2.00
2.01
2.01
2.00
2.16
2.18
2.03
3.48
3.03
f1 (ppm)


171.15
171.09
137.54
137.15
134.49
129.04
128.00
127.13
76.87
61.62
61.58
58.51
38.39
32.56
20.75
14.04
13.95
f1 (ppm)

Diethyl (4a*R*,9a*S*)-4a,9a-dihydroxy-4,10-diphenyl-3,4a,5,6,7,8,9,9a-octahydrocyclohepta[*f*]indene-2,2(1*H*)-dicarboxylate (**4.3c**)



The reaction was conducted with *cis*-cycloheptane-1,2-diol **4.1c** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethylacetate = 80:20) provided the title compound **4.3c** (108.5 mg, 0.21 mmol) in 70% yield as a pale yellow solid.

TLC (SiO_2): R_f = 0.27 (hexanes : ethyl acetate = 3:1).

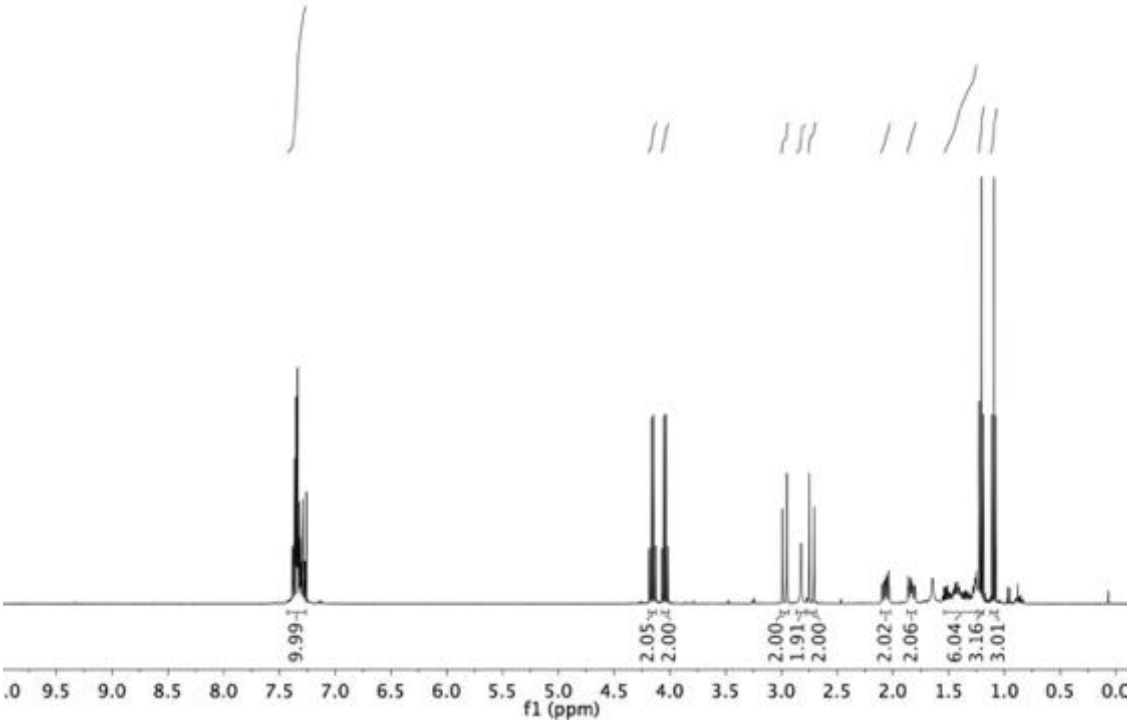
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.40-7.28 (m, 10H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.97 (d, *J* = 17.0 Hz, 2H), 2.82 (brs, 2H), 2.73, (d, *J* = 16.9 Hz, 2H), 2.07 (ddd, *J* = 14.3, 8.9, 2.4 Hz, 2H), 1.83 (ddd, *J* = 14.3, 8.9, 2.6 Hz, 2H), 1.23-1.54 (m, 6H), 1.21 (t, *J* = 7.1Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H) ppm.

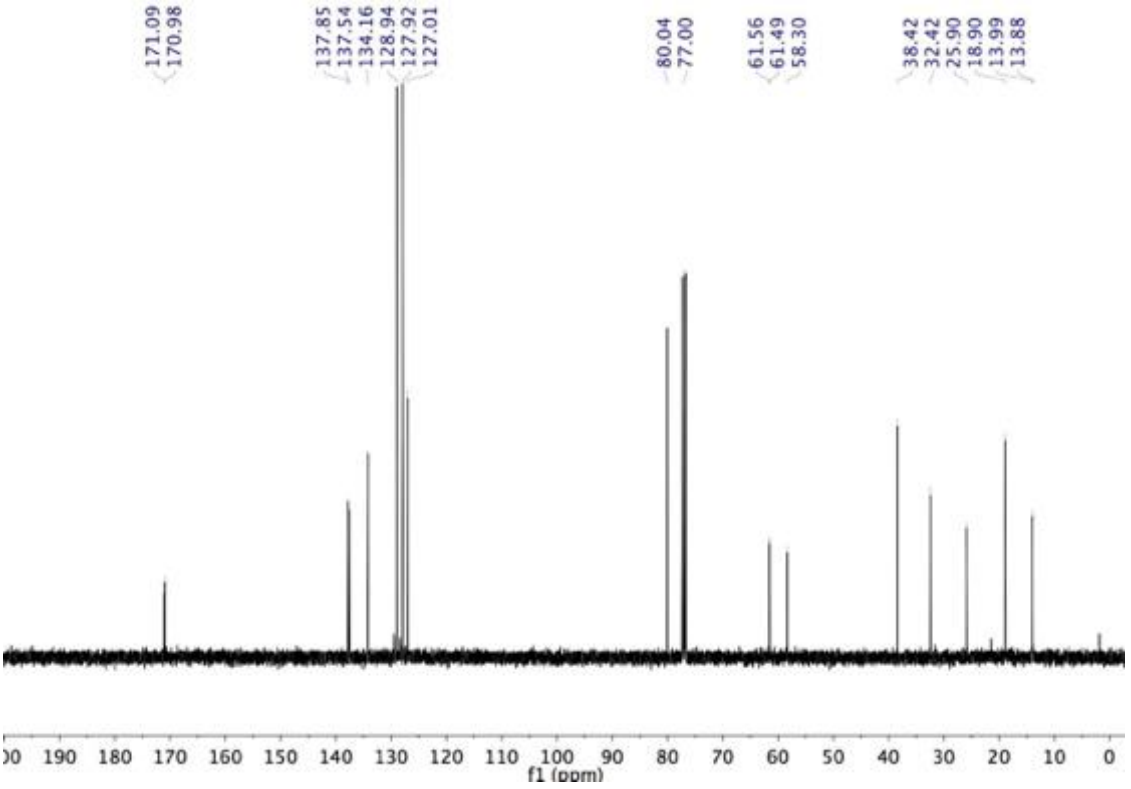
^{13}C NMR: (100 MHz, $CDCl_3$): δ =171.1, 171.0, 138.0, 137.6, 134.2, 129.0, 128.0, 127.0, 80.1, 61.6, 61.5, 58.3, 38.5, 32.5, 25.9, 18.9, 14.0, 13.9 ppm.

MP: 90 - 92 °C.

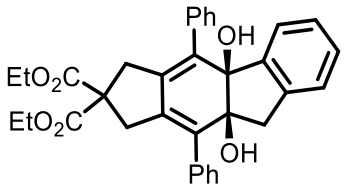
HRMS: (ESI) Calculated for $C_{32}H_{36}O_6$ [M+Na^+] = 539.24040, Found539.24090.

FTIR: (neat): 3521, 3054, 2927, 2857, 1727 cm^{-1}.


9.99
2.05
2.00
2.00
1.91
2.00
2.02
2.06
6.04
3.16
3.01
f1 (ppm)


171.09
170.98
137.85
137.54
134.16
128.94
127.92
127.01
80.04
77.00
61.56
61.49
58.30
38.42
32.42
25.90
18.90
13.99
13.88
f1 (ppm)

Diethyl (4a*R*,9a*S*)-4a,9a-dihydroxy-4,10-diphenyl-3,4a,9,9a tetrahydrocyclopenta[*b*]fluorine-2,2(1*H*)-dicarboxylate (**4.3d**)



The reaction was conducted with mixture of *cis*- and *trans*- 2,3-dihydro-1*H*-indene-1,2-diol **4.1d** in THF (0.3 mL, 1.0 M) in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3d** (130.4 mg, 0.24 mmol) in 81% yield as a pale yellow solid.

TLC (SiO_2): R_f = 0.20 (hexane : ethyl acetate = 3:1).

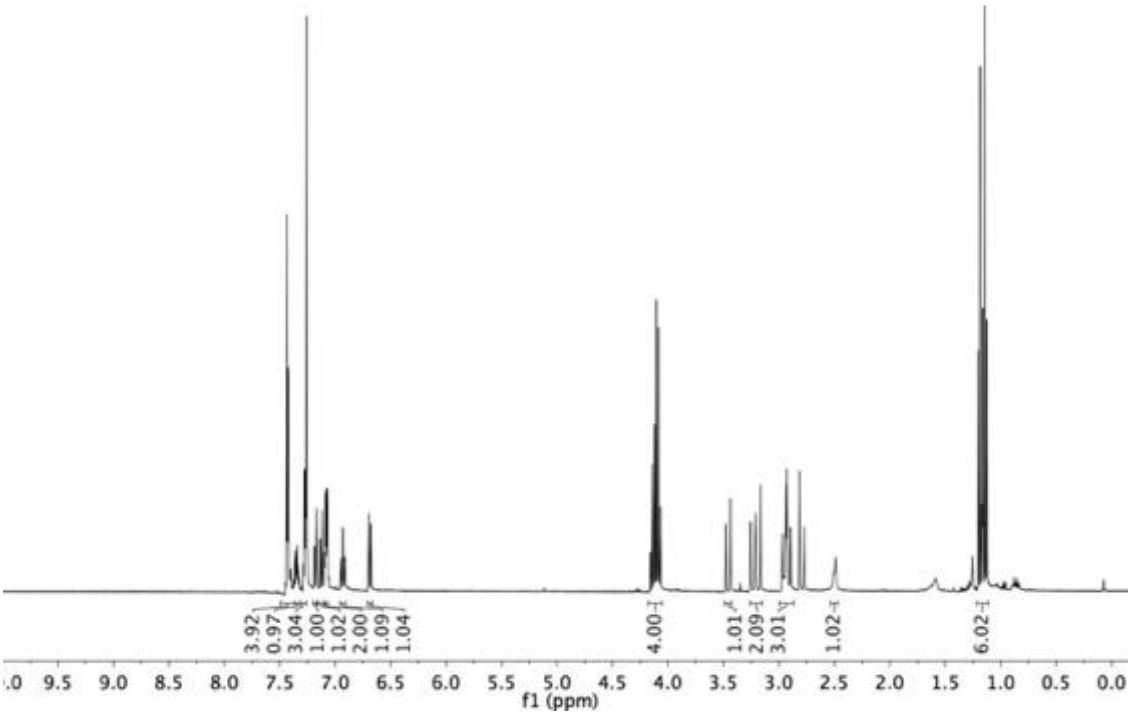
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.45-7.40 (m, 4H), 7.38-7.33 (m, 1H), 7.29-7.25 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 7.3 Hz, *J* = 1.1 Hz, 1H), 7.11-7.05 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.5, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.46 (d, *J* = 15.5 Hz, 1H), 3.24 (d, *J* = 15.5 Hz, 1H), 3.19 (d, *J* = 17.1 Hz, 1H), 2.98 (brs, 1H), 2.95 (dd, *J* = 17.1 Hz, *J* = 1.3 Hz, 1H), 2.91 (dd, *J* = 17.1 Hz, *J* = 1.3 Hz, 1H), 2.79 (d, *J* = 17.1 Hz, 1H), 2.49 (brs, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm

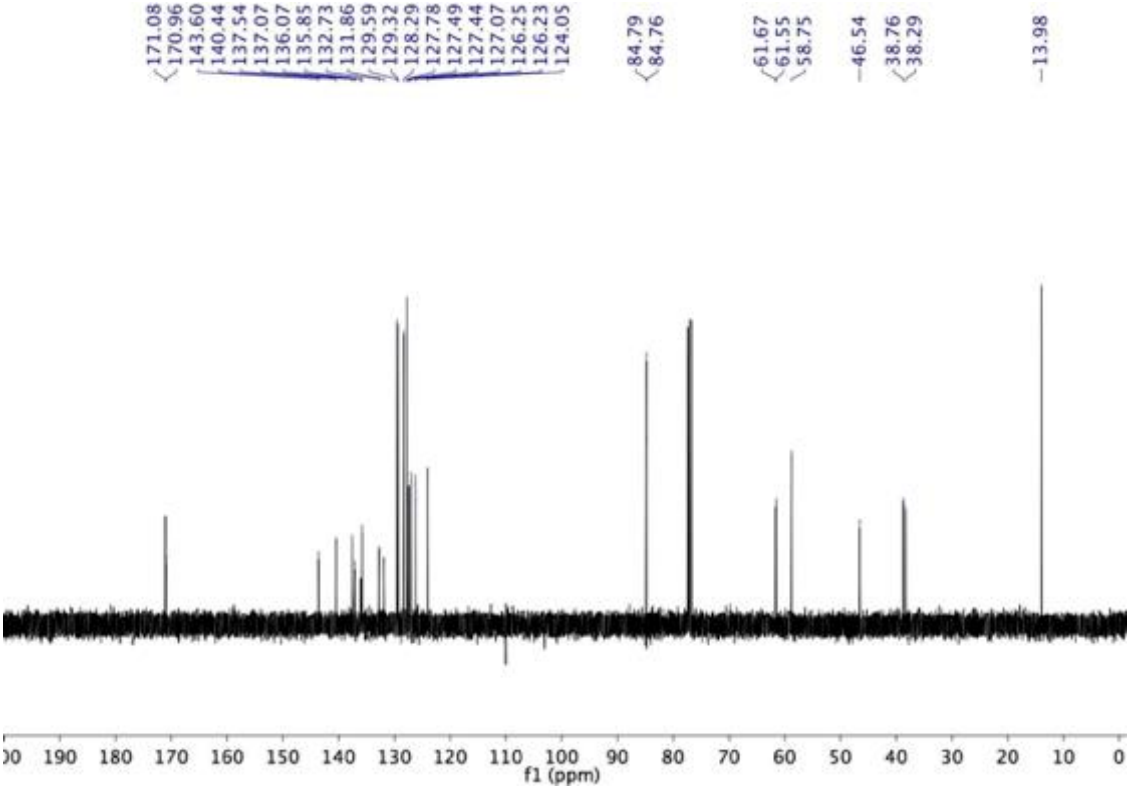
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.1, 171.0, 143.6, 140.4, 137.5, 137.1, 136.1, 135.9, 132.7, 131.9, 129.6, 129.3, 128.3, 127.8, 127.5, 127.4, 127.1,126.3, 126.2, 124.1, 84.8, 84.8, 61.7, 61.6, 58.8, 46.5, 38.8, 38.3, 14.0 ppm.

MP: 72 - 73 °C.

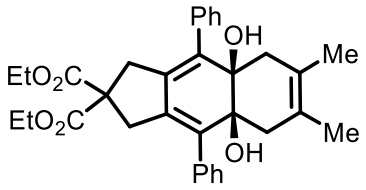
HRMS: (ESI) Calculated for $C_{34}H_{32}O_6$ [M+Na^+] = 559.20910, Found 559.20930.

FTIR: (neat): 3460, 3050, 2922, 2851, 1721 cm^{-1}.


3.92
0.97
3.04
1.00
1.02
2.00
1.09
1.04
4.00
1.01
2.09
3.01
1.02
6.02
f1 (ppm)


171.08
170.96
143.60
140.44
137.54
137.07
136.07
135.85
132.73
131.86
129.59
129.32
128.29
127.78
127.49
127.44
127.07
126.25
126.23
124.05
84.79
84.76
61.67
61.55
58.75
46.54
38.76
38.29
13.98
f1 (ppm)

Diethyl (4a*R*,8a*S*)-4a,8a-dihydroxy-6,7-dimethyl-4,9-diphenyl-1,3,4a,5,8,8a-hexahydro-2*H*-cyclopenta[*b*]naphthalene-2,2-dicarboxylate (**4.3e**)



The reaction was conducted with mixture of *cis*- and *trans*- 4,5-dimethylcyclohex-4-ene-1,2-diol **4.1e** in accordance with the general procedure. Flash column chromatography (SiO_2, Et_2O:DCM = 1.5:98.5 to 3:97 with 0.1% NEt_3) provided the title compound **4.3e** (95.2 mg, 0.18 mmol) in 60% yield as a pale yellow oil.

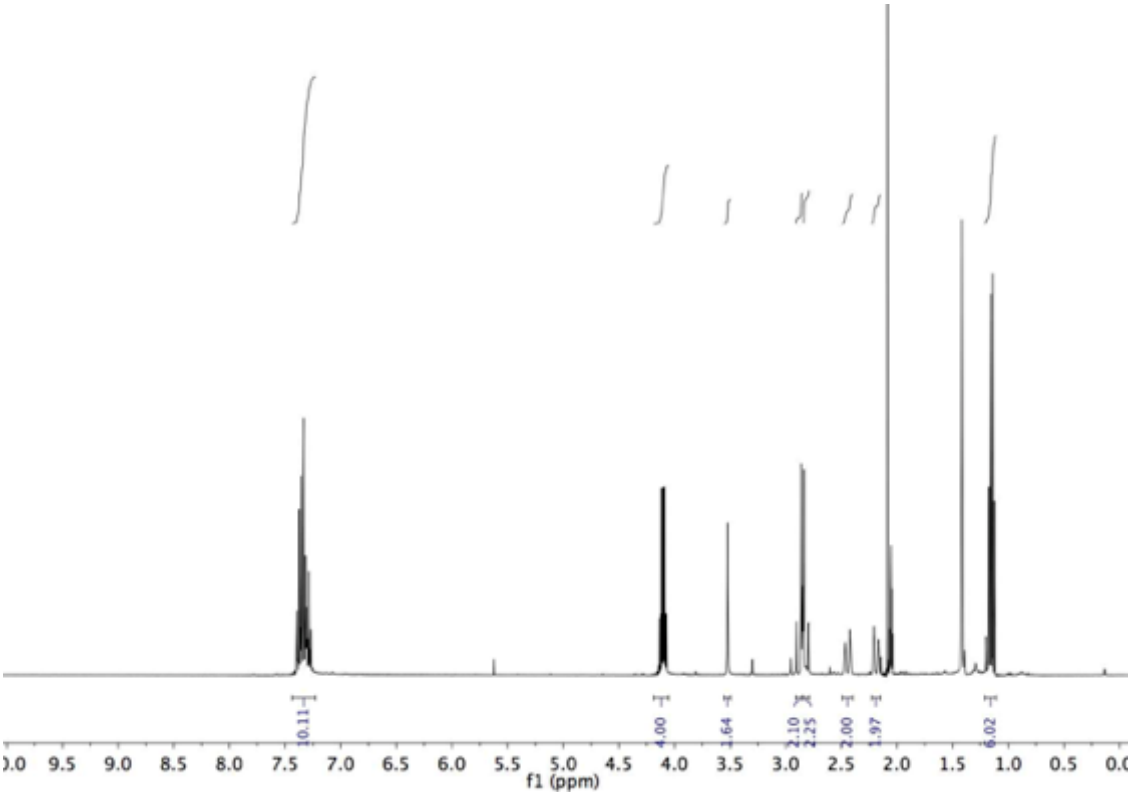
TLC (SiO_2): R_f = 0.40 (hexanes : ethyl acetate = 2:1).

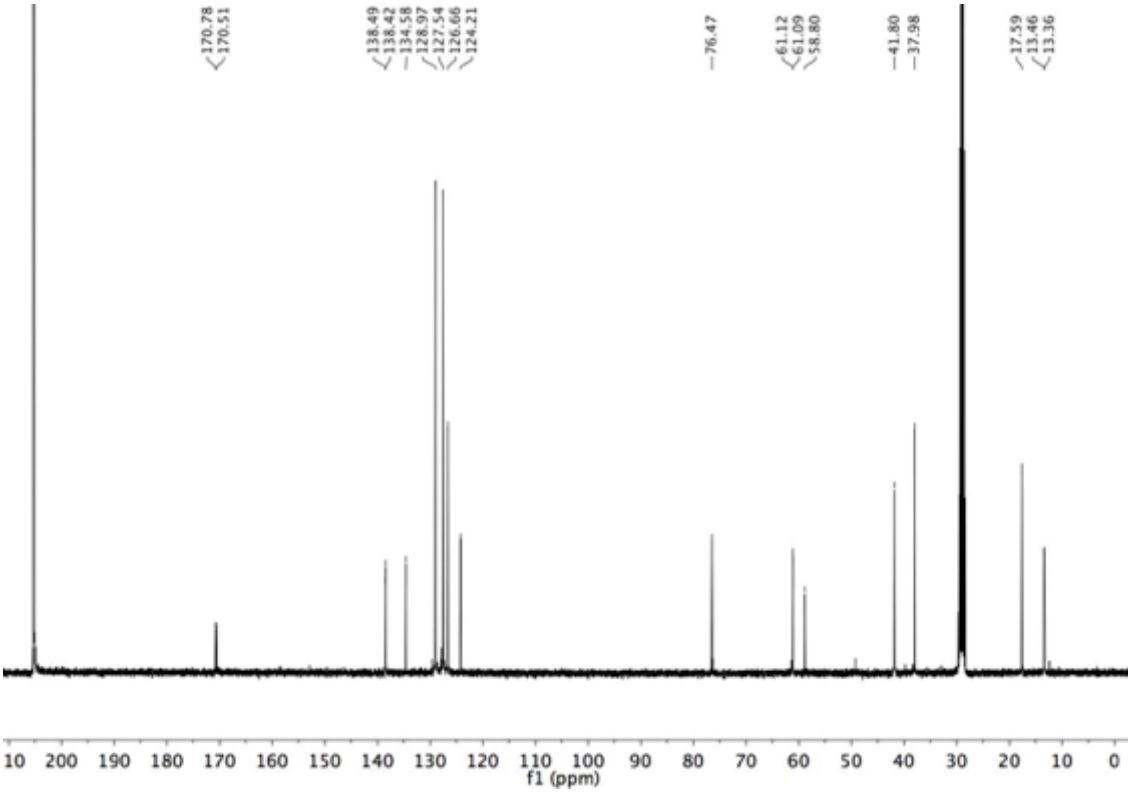
^{1}H NMR: (400 MHz, *d*-Acetone): δ = 7.39-7.27 (m, 10H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.52 (s, 2H), 2.88 (d, *J* = 17.1 Hz, 2H), 2.81 (d, *J* = 17.1 Hz, 2H), 2.44 (d, *J* = 16.4 Hz 2H), 2.18 (d, *J* = 16.4 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm

^{13}C NMR: (100 MHz, *d*-Acetone): δ =170.8, 170.5, 138.5. 138.4, 134.6, 129.0, 127.5, 126.7, 124.2, 76.5, 61.1, 61.1, 58.8, 41.8, 38.0, 17.6, 13.5, 13.4 ppm.

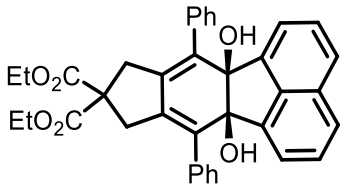
HRMS: (ESI) Calculated for $C_{33}H_{36}O_6$ [M+Na^+] = 551.24040, Found 551.24170.

FTIR: (neat): 3477, 2983, 2911, 1727 cm^{-1}.


10.11
4.00
1.64
2.10
2.25
2.00
1.97
6.02
f1 (ppm)


170.78
170.51
138.49
138.42
134.58
128.97
127.54
126.66
124.21
76.47
61.12
61.09
58.80
41.80
37.98
17.59
13.46
13.36
f1 (ppm)

Diethyl (6b*R*,11a*S*)-6b,11a-dihydroxy-7,11-diphenyl-6b,8,10,11a-tetrahydro-9*H*-cyclopenta[*k*]fluoranthene-9,9-dicarboxylate (**4.3f**)



The reaction was conducted with mixture of *cis*- and *trans*- 1,2-dihydroacenaphthylene-1,2-diol **4.1f** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3f** (137.4 mg, 0.24 mmol) in 80% yield as a pale yellow solid.

TLC (SiO_2): R_f = 0.14 (hexanes : ethyl acetate = 3:1).

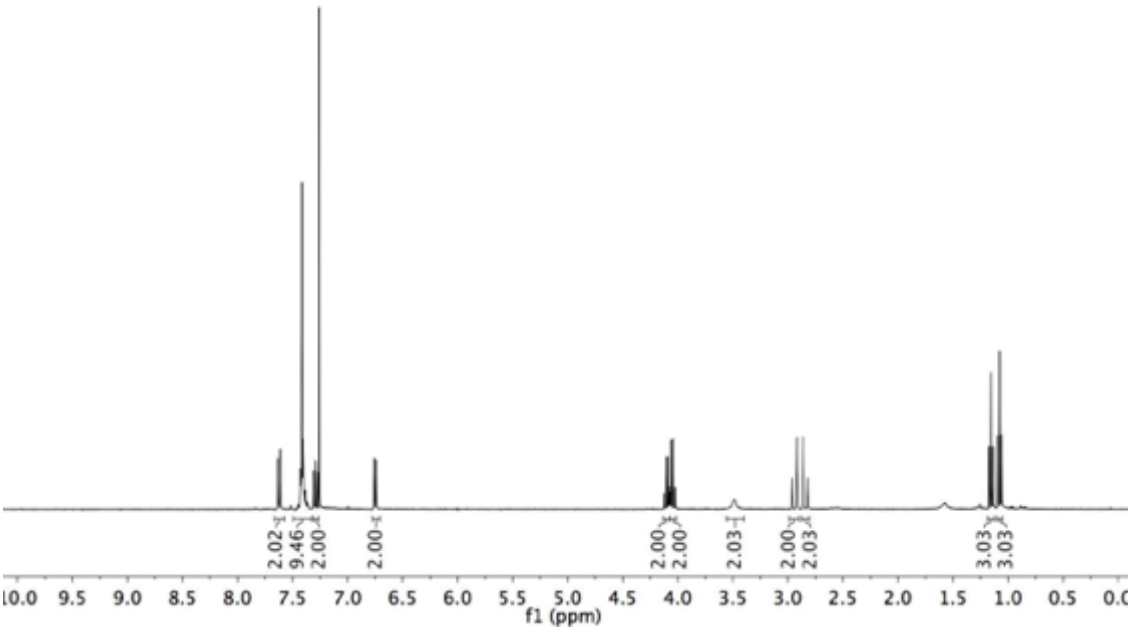
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 8.4, *J* = 0.7 Hz, 2H), 7.45-7.36 (m, 10H), 7.29 (dd, *J* = 8.2, 7.1 Hz, 2H), 6.75 (dd, *J* = 7.1, 0.7 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.94 (d, *J* = 16.9 Hz, 2H), 2.84 (d, *J* = 16.9 Hz, 2H), 2.46 (brs, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), ppm.

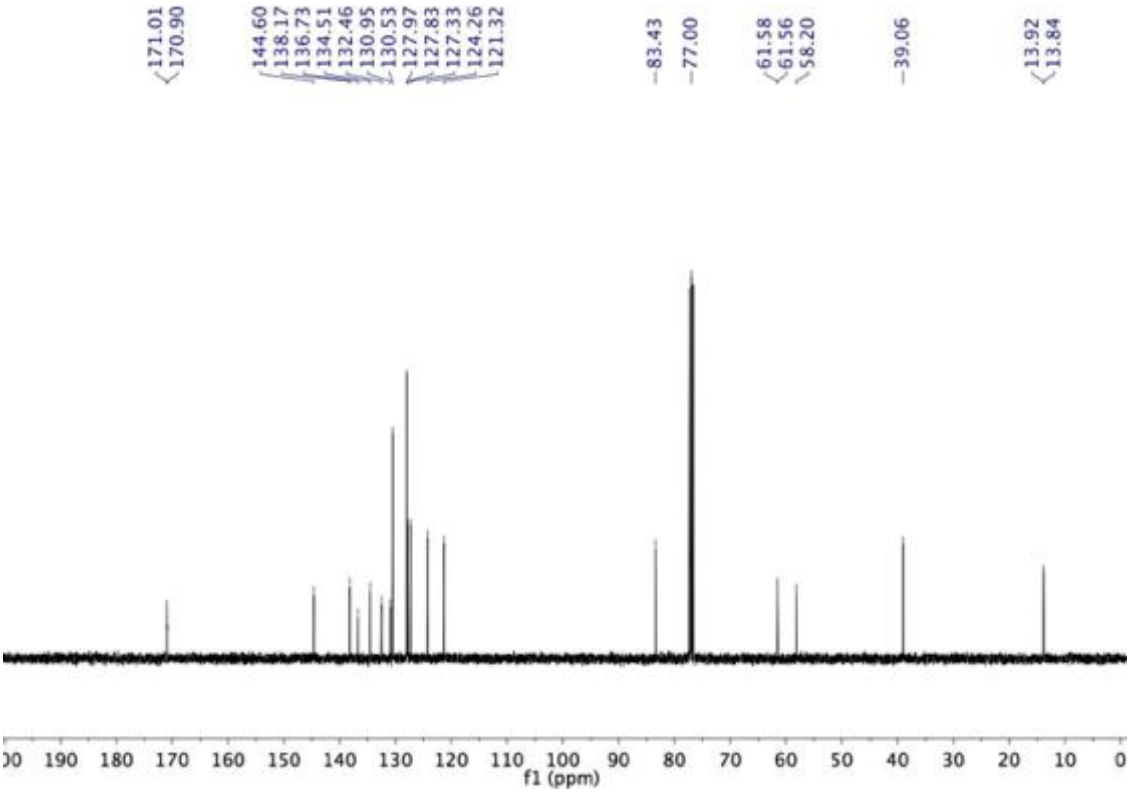
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.0, 170.9, 144.6, 138.2, 136.7, 134.5, 132.5, 131.0, 130.5, 127.9, 127.8, 127.3, 124.3, 121.3, 83.4, 61.6, 61.6, 58.2, 39.1, 13.9, 13.8 ppm.

MP: 190 - 192 °C.

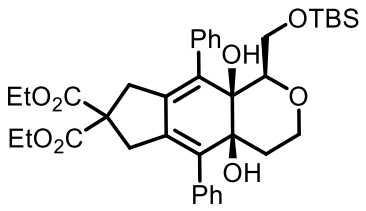
HRMS: (ESI) Calculated for $C_{37}H_{32}O_6$ [M+Na^+] = 595.20910, Found 595.20900.

FTIR: (neat): 3521, 3054, 2927, 2857, 1727 cm^{-1}.


2.02
9.46
2.00
2.00
2.00
2.00
2.03
2.00
2.03
3.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.01
170.90
144.60
138.17
136.73
134.51
132.46
130.95
130.53
127.97
127.83
127.33
124.26
121.32
83.43
77.00
61.58
61.56
58.20
39.06
13.92
13.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Diethyl (1*R*,4a*S*,9a*S*)-1-(((*tert*-butyldimethylsilyl)oxy)methyl)-4a,9a-dihydroxy-5,9-diphenyl-3,4,4a,6,8,9a-Hexahydrocyclopenta[*g*]isochromene-7,7(1*H*)-dicarboxylate (**4.3g**)



The reaction was conducted with (2*R*,3*S*,4*R*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4-diol **4.1g** in accordance with the general procedure. Flash column chromatography (SiO_2, Et_2O:DCM = 1:99 to 2:98 with 0.1% NEt_3) provided the title compound **4.3g** (112.9 mg, 0.12 mmol, dr = 5.4:1) in 58% yield as a slightly yellow oil. (NOTE: Tentative relative configuration is provided.)

TLC (SiO_2): R_f = 0.30 (hexanes : ethyl acetate = 1:5).

^{1}H NMR: (400 MHz, *d*-Acetone):

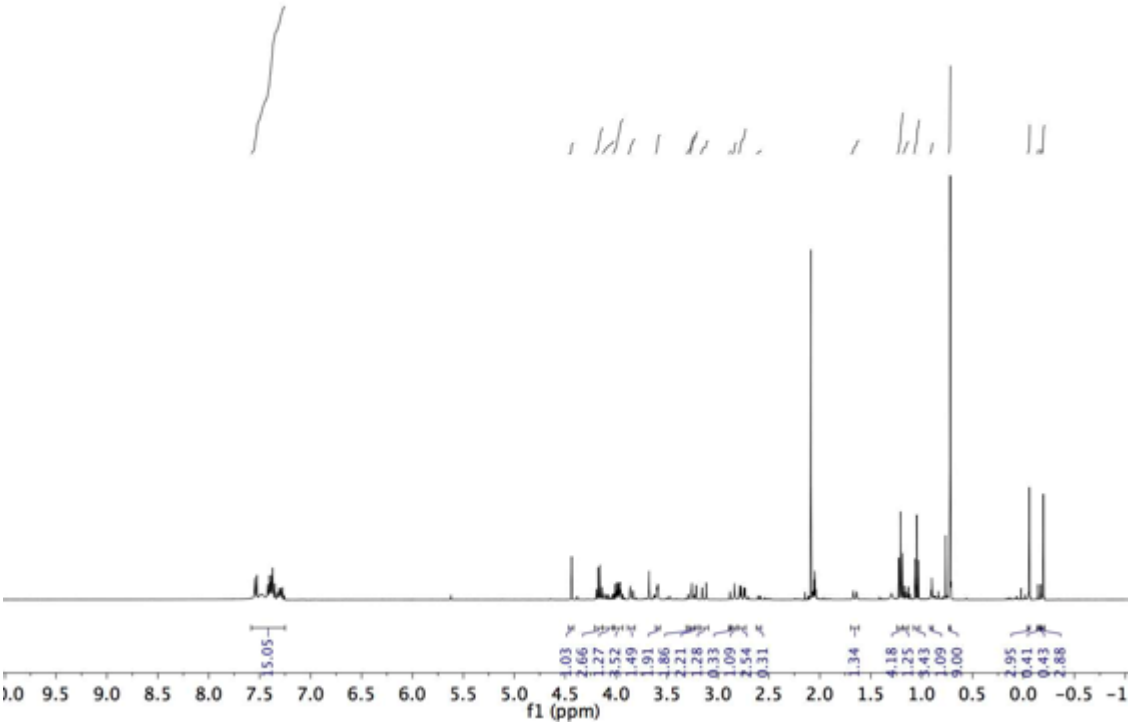
Major diastereomer: δ = 7.55-7.25 (m, 10H), 4.44 (s, 1H), 4.18 (t, *J* = 7.2 Hz, 2H), 4.04-3.97 (m, 2H), 3.87-3.83 (m, 1H), 3.63-3.59 (m, 2H), 3.25 (d, *J* = 17.2 Hz, 1H), 3.20 (d, *J* = 17.2 Hz, 1H), 2.84 (s, 1H), 2.75 (dd, *J* = 16.5, 4.9 Hz, 2H), 1.66 (d, *J* = 7.2 Hz, 1H) 1.20 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.72 (s, 9H), -0.05 (s, 3H), -0.19 (s, 3H) ppm.

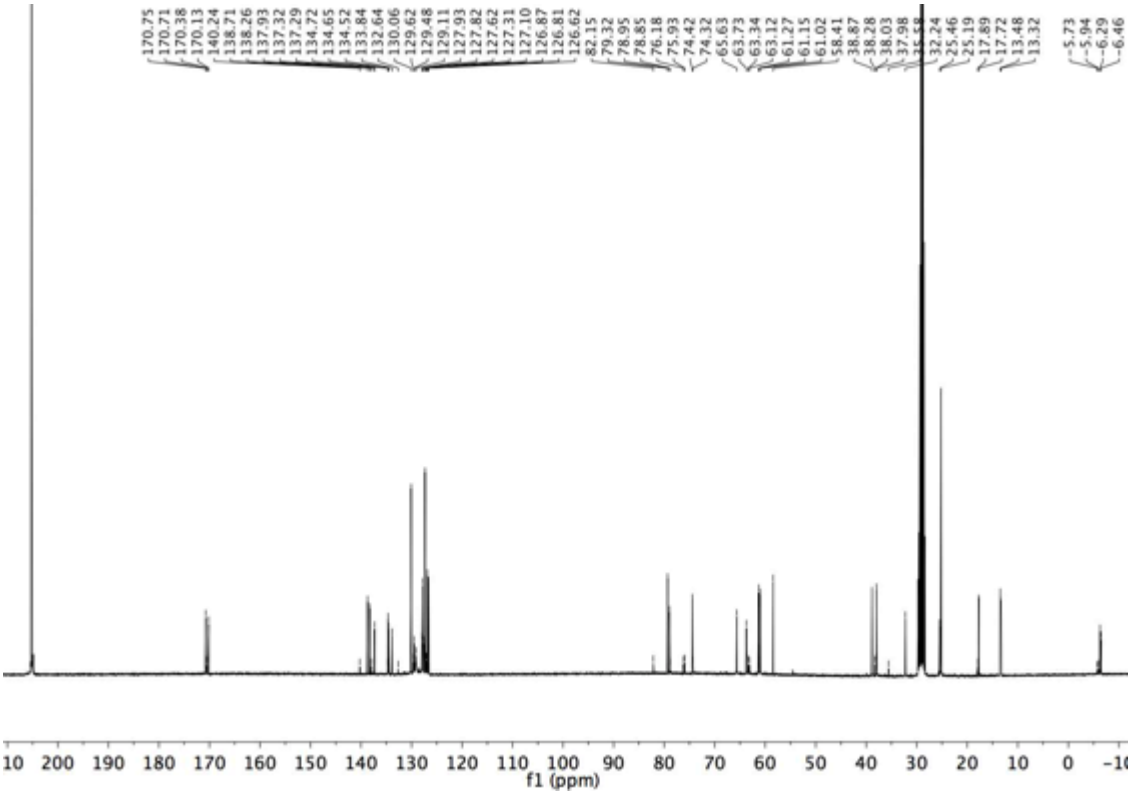
Minor diastereomer: δ = 7.55-7.25 (m, 10H), 4.38 (s, 1H), 4.14-3.95 (m, 5H), 3.62 (dd, *J* = 2.3, 2.1 Hz), 3.51-3.49 (m, 1H), 3.48-3.46 (m, 2H), 2.88 (s, 1H), 1.66 (d, *J* = 7.2 Hz, 2H) 1.18 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.76 (s, 9H), -0.14 (s, 3H), -0.17 (s, 3H) ppm.

^{13}C NMR: (100 MHz, *d*-Acetone): δ = 170.8, 170.1, 138.7, 138.3, 137.3, 134.7, 132.7, 133.8, 130.1, 129.1, 127.8, 127.3, 126.9, 126.6, 79.3, 79.0, 74.4, 65.6, 63.7, 61.3, 61.0, 38.9, 38.0, 32.2, 25.5, 25.2, 17.7, 13.5, 13.3, -6.3, -6.5 ppm

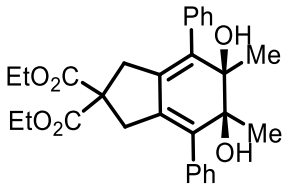
HRMS: (ESI) Calculated for $C_{37}H_{48}O_8Si$ [M+Na^+] = 671.30110, Found 671.30330.

FTIR: (neat): 3430, 2929, 2856, 1729 cm^{-1}.


15.05
1.03
2.66
1.27
3.52
1.49
1.91
1.86
2.21
1.28
0.33
1.09
2.54
0.31
1.34
4.18
1.25
3.43
1.09
9.00
2.95
0.41
0.43
2.88
f1 (ppm)


170.75
170.71
170.38
170.13
140.24
138.71
138.26
137.93
137.32
137.29
134.72
134.65
134.52
133.84
132.64
130.06
129.62
129.48
129.11
127.93
127.82
127.62
127.31
127.10
126.87
126.81
126.62
82.15
79.32
78.95
78.85
76.18
75.93
74.42
74.32
65.63
63.73
63.34
63.12
61.27
61.15
61.02
58.41
38.87
38.28
38.03
37.98
35.58
32.24
25.46
25.19
17.89
17.72
13.48
13.32
5.73
5.94
6.29
6.46
f1 (ppm)

Diethyl (5*R*,6*S*)-5,6-dihydroxy-5,6-dimethyl-4,7-diphenyl-1,3,5,6-tetrahydro-2*H*-indene-2,2-dicarboxylate (**4.3h**)



The reaction was conducted with (2*R*,3*R*)-butane-2,3-diol **4.1h** in accordance with the general procedure. Flash column chromatography (SiO_2, Et_2O:DCM = 1.5:98.5 to 3:97 with 0.1% NEt_3) provided the title compound **4.3h** (123.0 mg, 0.26 mmol) in 86% yield as a colorless oil.

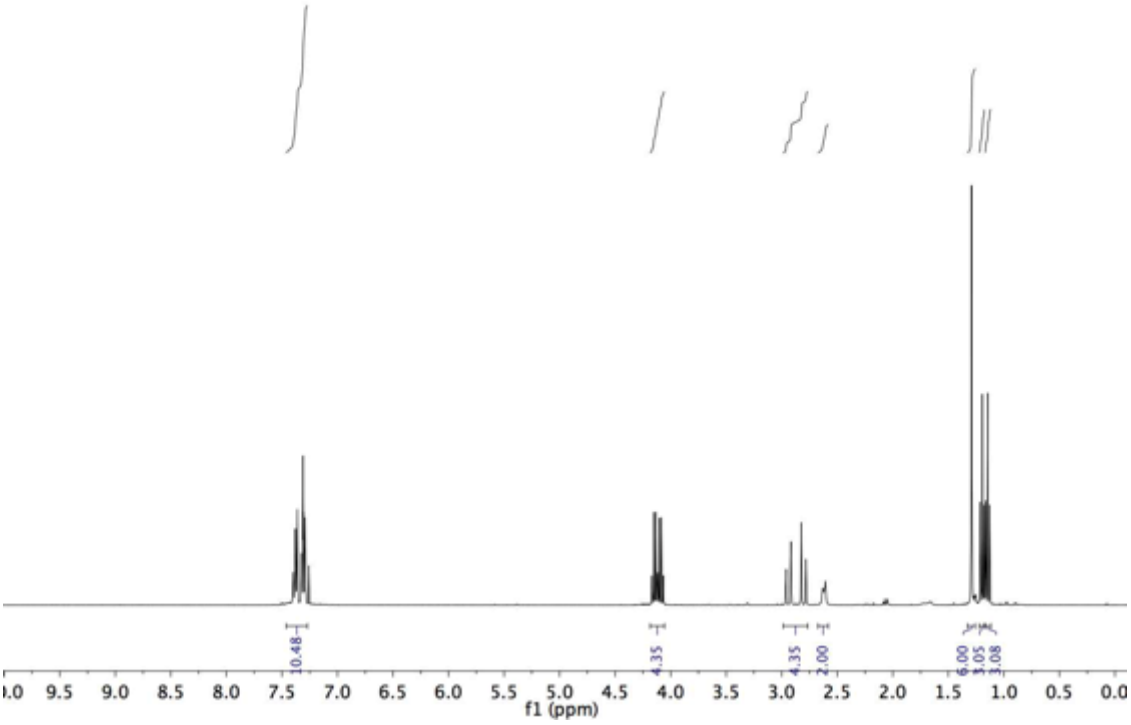
TLC (SiO_2): R_f = 0.40 (hexanes : ethyl acetate = 2:1).

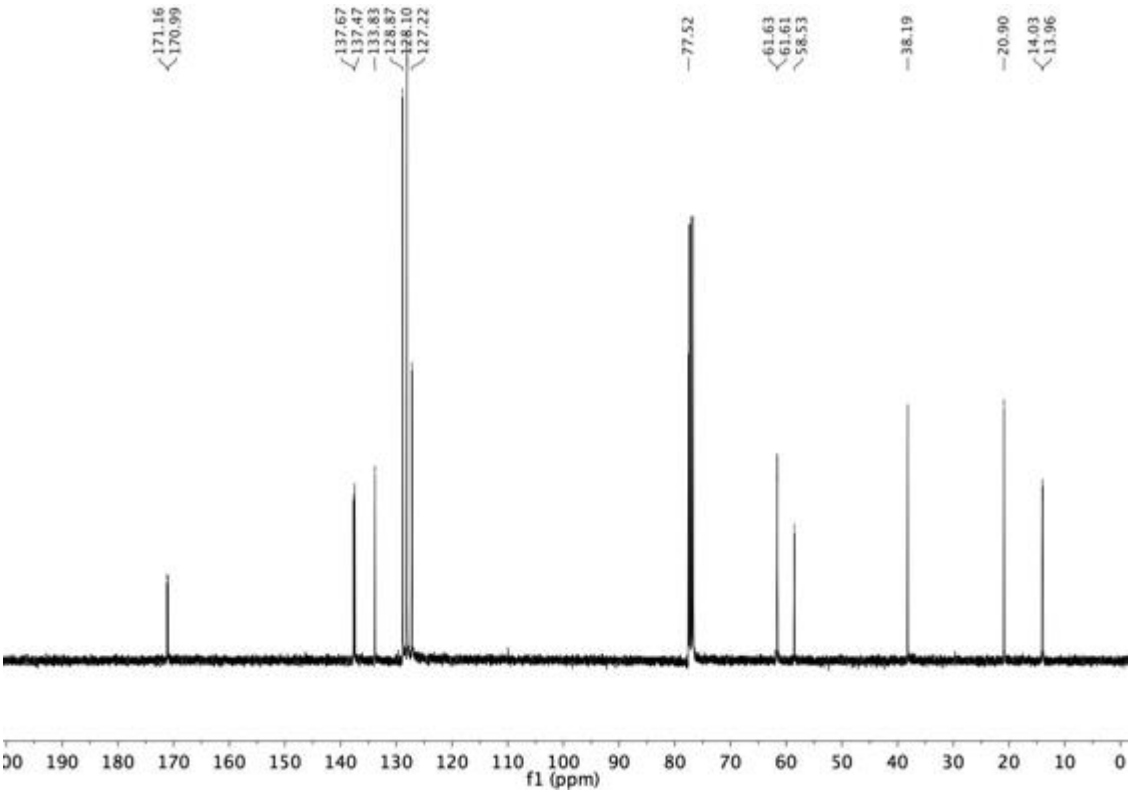
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.45-7.28 (m, 10H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.94 (d, *J* = 17.1 Hz, 2H), 2.80 (d, *J* = 17.1 Hz, 2H), 2.61 (brs, 2H), 1.29 (s, 6H), 1.20 (d, *J* = 7.2 Hz 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.2, 171.0, 137.7, 137.5, 133.8, 238.9, 128.1, 127.2, 77.5, 61.6, 61.6, 58.5, 38.2, 20.9, 14.0, 14.0 ppm.

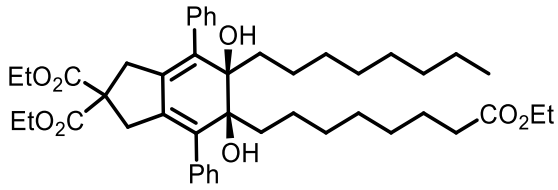
HRMS: (ESI) Calculated for $C_{29}H_{32}O_6$ [M+Na^+] = 499.20910, Found499.21030.

FTIR: (neat): 3501, 2984, 1726 cm^{-1}.


10.48
4.35
4.35
2.00
6.00
3.05
3.08
f1 (ppm)


171.16
170.99
137.67
137.47
133.83
128.87
128.10
127.22
77.52
61.63
61.61
58.53
38.19
20.90
14.03
13.96
f1 (ppm)

Diethyl (5*S*,6*R*)-5-(8-ethoxy-8-oxooctyl)-5,6-dihydroxy-6-octyl-4,7-diphenyl-1,3,5,6-tetrahydro-2*H*-indene-2,2-dicarboxylate (**4.3i**)



The reaction was conducted with mixture of ethyl (9*R*,10*S*)-9,10-dihydroxyoctadecanoate and ethyl (9*S*,10*R*)-9,10-dihydroxyoctadecanoate **4.1i** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3i** (142.5 mg, 0.20 mmol) in 65% yield as yellow oil.

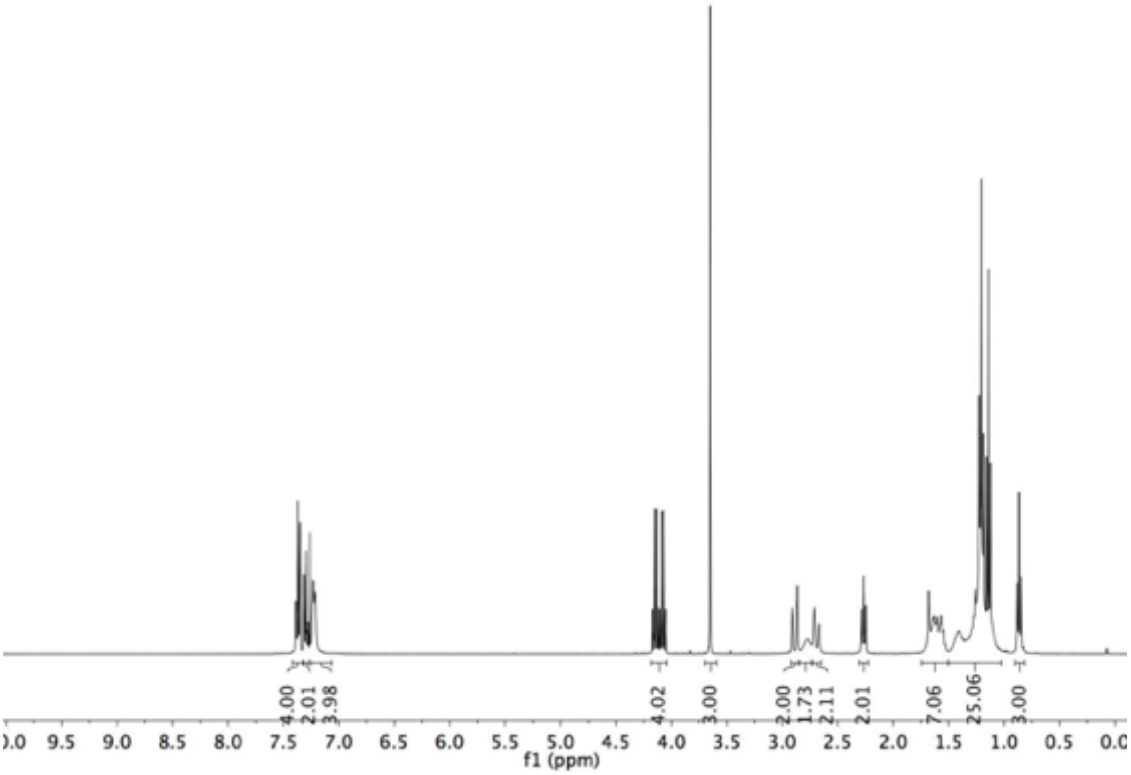
TLC (SiO_2): R_f = 0.26 (hexane : ethyl acetate = 4:1).

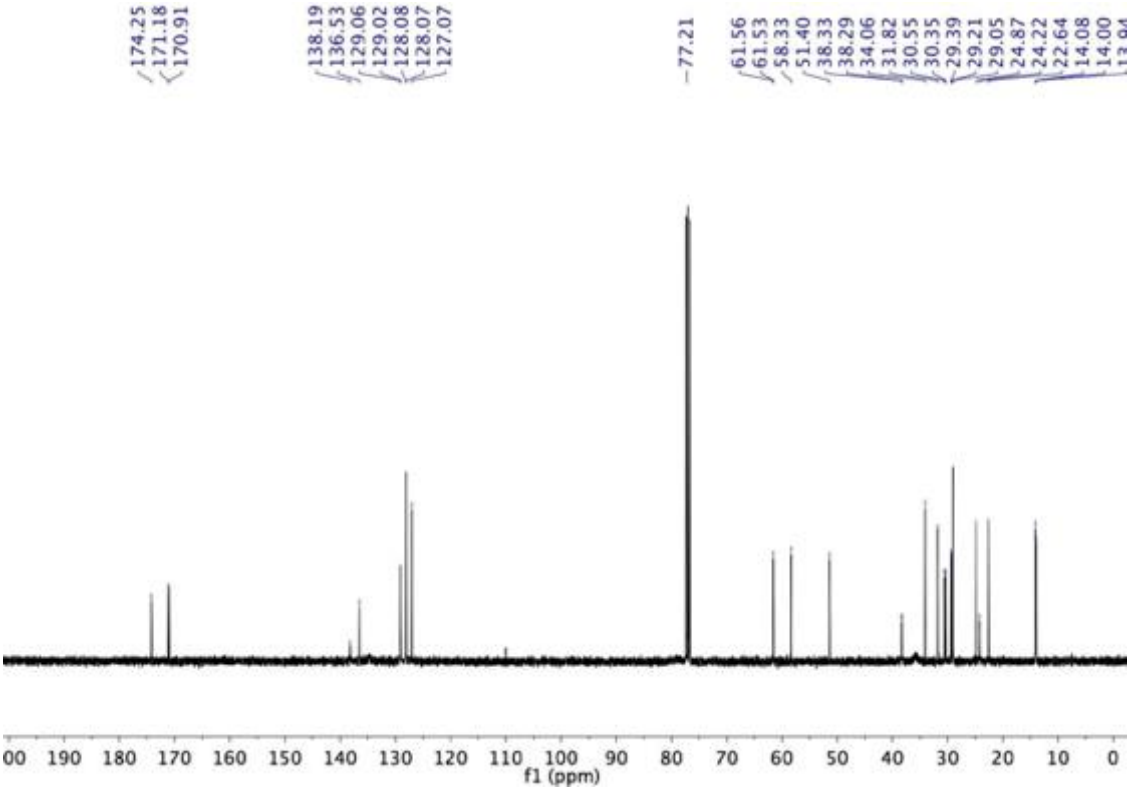
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.45-7.34 (m, 4H), 7.33-7.27 (m, 2H), 7.25-7.14 (m, 4H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.89 (d, *J* = 16.9 Hz, 2H), 2.78 (brs, 2H), 2.69 (d, *J* = 16.9 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 3H), 1.74-1.53 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.50-1.10 (m, 19H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 174.3, 171.2, 170.9, 138.2, 136.5, 129.1, 129.0, 128.1, 128.1, 61.6, 61.5, 58.3, 51.4, 38.3, 38.3, 34.1, 31.9, 30.6, 30.4, 29.4, 29.2, 29.1, 24.9, 24.2, 24.2, 22.6, 14.1, 14.0, 13.9 ppm.

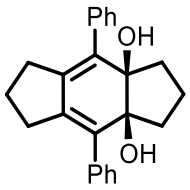
HRMS: (ESI) Calculated for $C_{44}H_{60}O_8$ [M+Na^+] = 739.41800, Found 739.41990.

FTIR: (neat): 3509, 2926, 2853, 1730, 1598 cm^{-1}.


4.00
2.01
3.98
4.02
3.00
2.00
1.73
2.11
2.01
7.06
25.06
3.00
f1 (ppm)


174.25
171.18
170.91
138.19
136.53
129.06
129.02
128.08
128.07
127.07
77.21
61.56
61.53
58.33
51.40
38.33
38.29
34.06
31.82
30.55
30.35
29.39
29.21
29.05
24.87
24.22
22.64
14.08
14.00
f1 (ppm)

(3a*R*,8a*S*)-4,8-Diphenyl-2,3,6,7-tetrahydro-*s*-indacene-3a,8a(1*H*,5*H*)-diol (4.3j)



The reaction was conducted with diyne **4.2b** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 75:25) provided the title compound **4.3j** (87.8 mg, 0.26 mmol) in 85% yield as a pale yellow solid.

TLC (SiO_2): R_f = 0.26 (hexanes : ethyl acetate = 4:1).

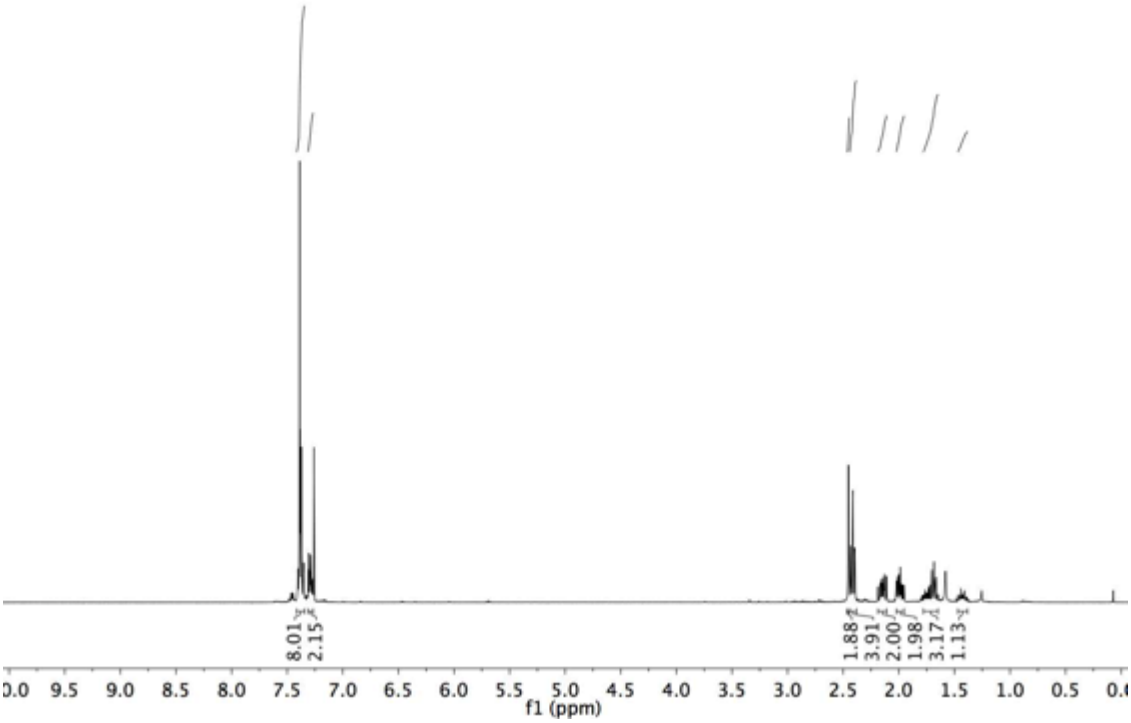
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.43-7.33 (m, 8H), 7.32-7.27 (m, 2H), 2.45 (s, 2H), 2.41 (dt, *J* = 7.3, 1.3 Hz, 4H), 2.15 (ddd, *J* = 13.4, 9.7, 7.3 Hz, 2H), 1.99 (ddd, *J* = 13.4, 9.7, 4.5 Hz, 2H), 1.64-1.87 (m, 3H), 1.46-1.44 (m, 1H), ppm.

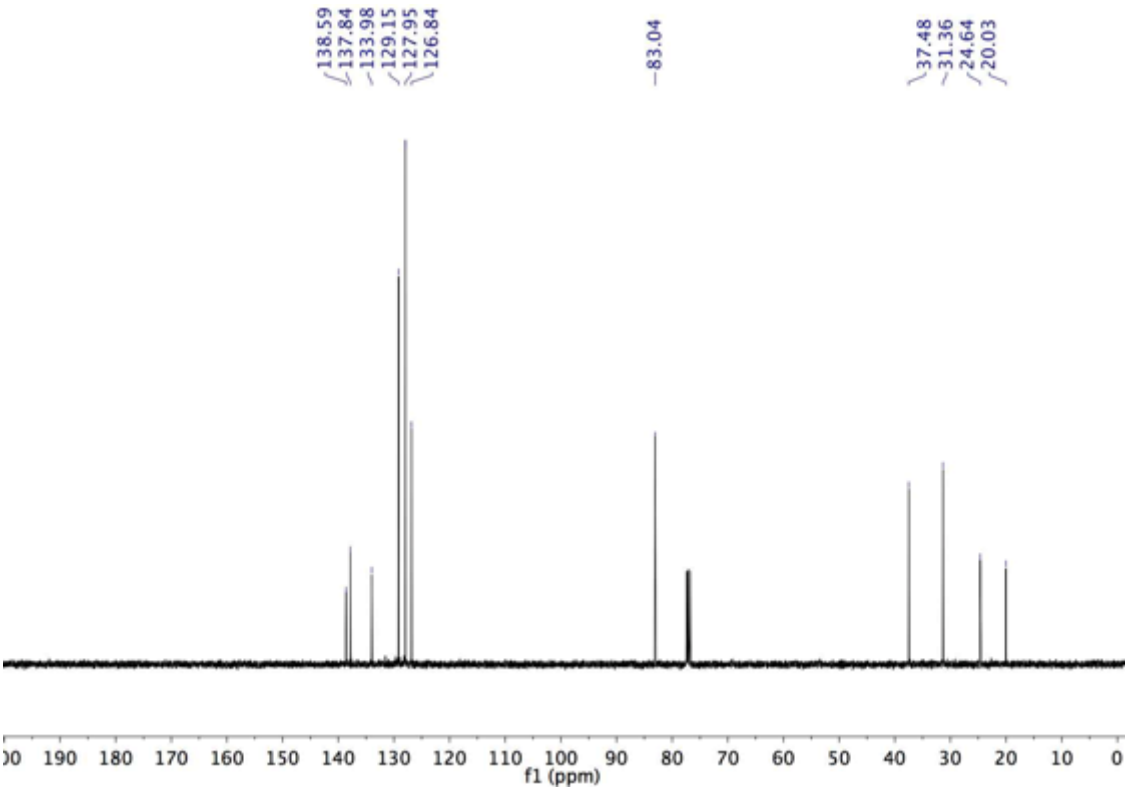
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 138.6, 137.8, 134.0, 129.2, 128.0, 126.8, 83.0, 37.5, 31.4, 24.6, 20.0 ppm.

MP: 140 - 142 °C.

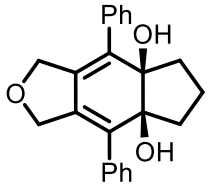
HRMS: (ESI) Calculated for $C_{24}H_{24}O_2$ [M+Na^+] = 367.16690, Found 367.16740.

FTIR: (neat): 3359, 3057, 3016, 2965, 2848 cm^{-1}.


8.01
2.15
1.88
3.91
2.00
1.98
3.17
1.13
f1 (ppm)


138.59
137.84
133.98
129.15
127.95
126.84
83.04
37.48
31.36
24.64
20.03
f1 (ppm)

(4a*R*,7a*S*)-4,8-Diphenyl-6,7-dihydro-1*H*-indeno[5,6-*c*]furan-4a,7a(3*H*,5*H*)-diol (4.3k)



The reaction was conducted with diyne **4.2c** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3k** (85.2 mg, 0.25 mmol) in 82% yield as a brown solid.

TLC (SiO_2): R_f = 0.26 (hexanes : ethyl acetate = 3:1).

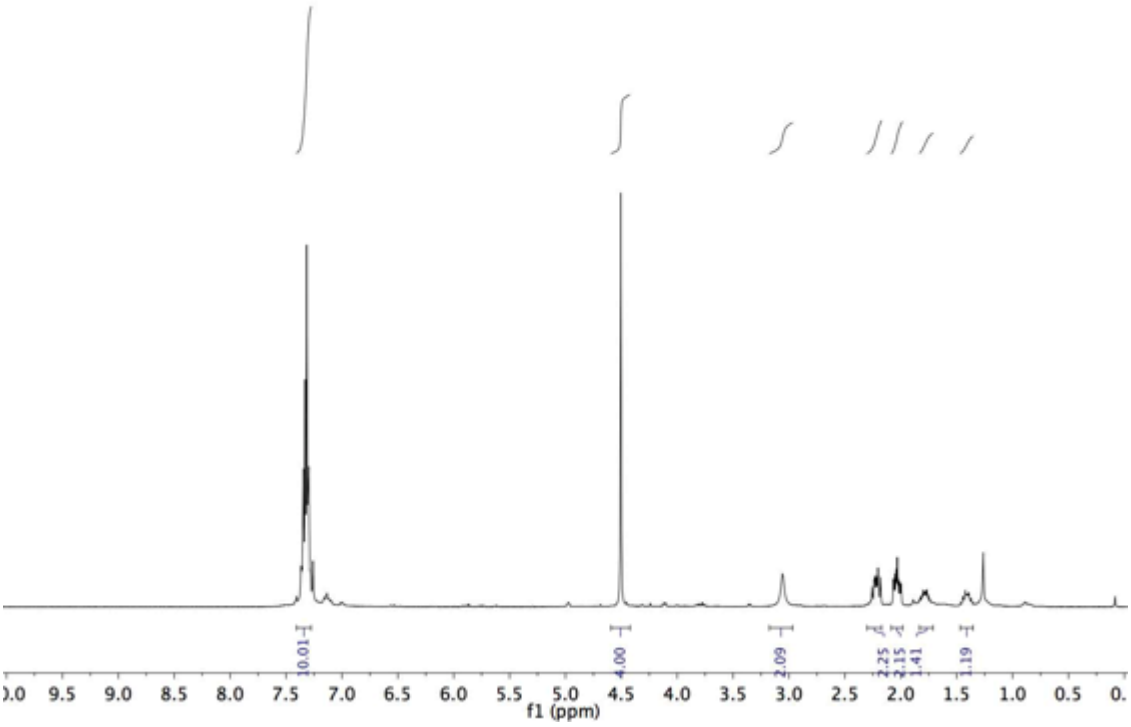
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.39-7.28 (m, 10H), 4.51 (s, 4H), 3.13-2.97 (br, 2H), 2.28-2.16 (m, 2H), 2.08-1.98 (m, 2H), 1.84-1.74 (m, 1H), 1.45-1.38 (m, 1H) ppm.

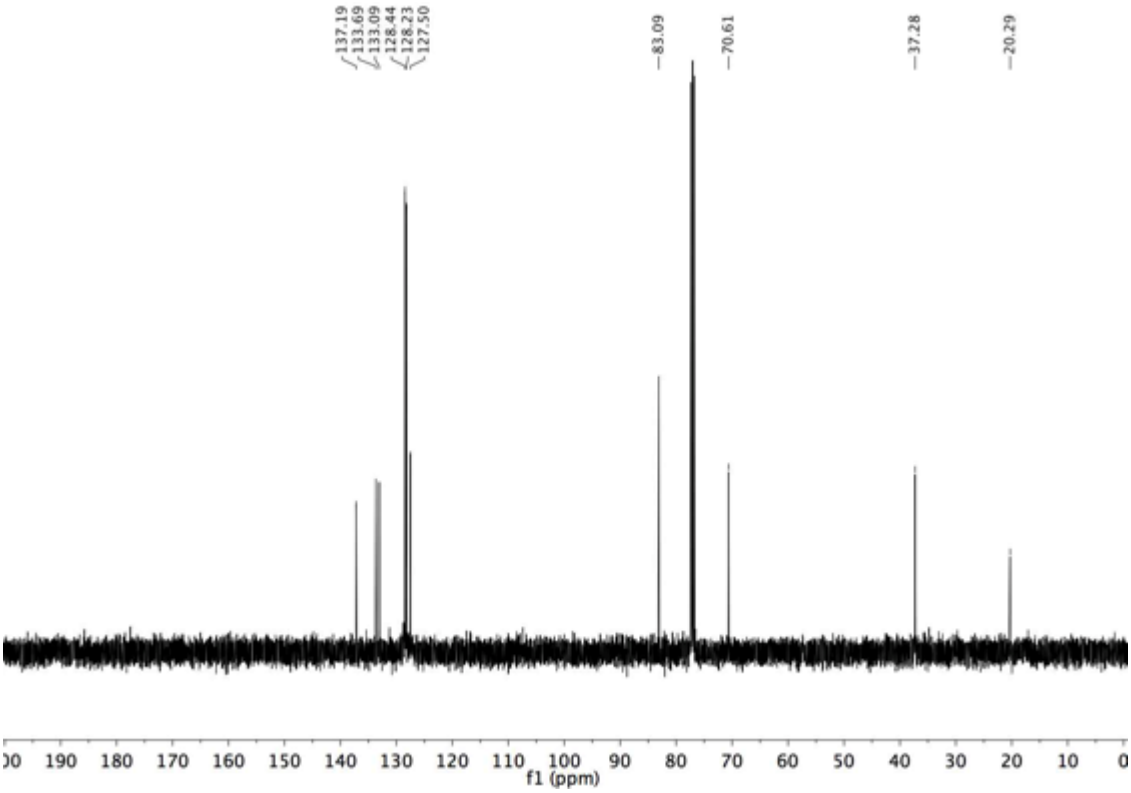
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 137.2, 133.7, 133.1, 128.4, 128.2, 127.5, 83.1, 70.6, 37.3, 20.3 ppm.

MP: 171 - 173 °C.

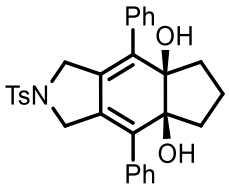
HRMS: (ESI) Calculated for $C_{23}H_{22}O_3$ [M+Na^+] =369.14610, Found 369.14670.

FTIR: (neat): 3298, 2930, 2362 cm^{-1}.


10.01
4.00
2.09
2.25
2.15
1.41
1.19
f1 (ppm)


137.19
133.69
133.09
128.44
128.23
127.50
83.09
70.61
37.28
20.29
f1 (ppm)

(4a*R*,7a*S*)-4,8-Diphenyl-2-tosyl-2,3,6,7-tetrahydrocyclopenta[*f*]isoindole-4a,7a(1*H*,5*H*)-diol (4.3l)



The reaction was conducted with diyne **4.2d** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 70:30) provided the title compound **4.3l** (97.4 mg, 0.20 mmol) in 65% yield as a brown solid.

TLC (SiO_2): R_f = 0.25 (hexanes : ethyl acetate = 2:1).

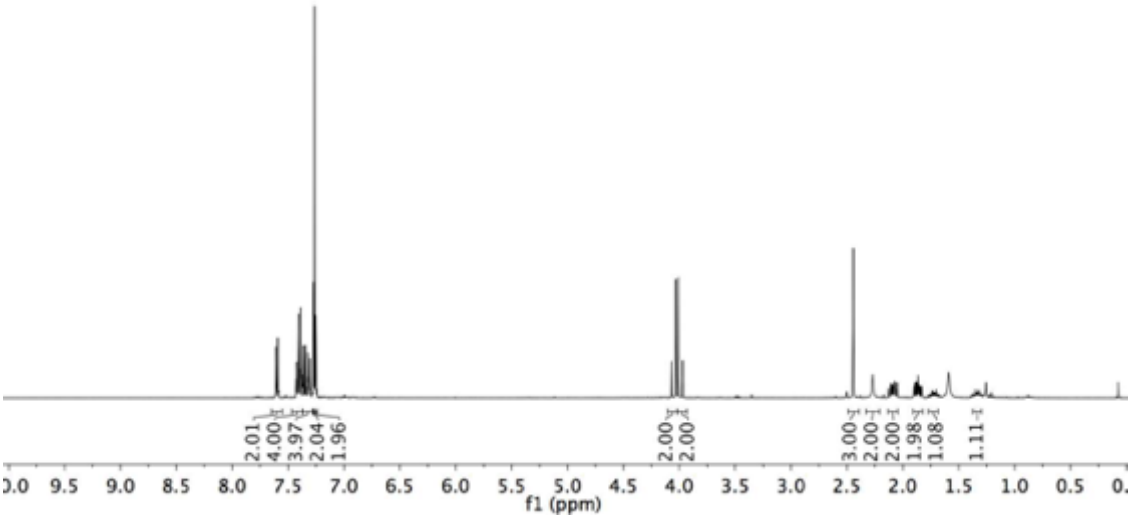
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.63-7.57 (m, 2H), 7.43-7.38 (m, 4H), 7.37-7.31 (m, 4H), 7.28-7.27 (m, 2H), 7.25-7.24 (m, 2H), 4.05 (d, *J* = 15.1 Hz, 2H), 3.99 (d, *J* = 15.1 Hz, 2H), 2.44 (s, 3H), 2.27 (brs, 2H), 2.09 (ddd, *J* = 13.7, 9.5, 7.4 Hz, 2H), 1.87 (ddd, *J* = 13.7, 9.5, 4.5 Hz, 2H), 1.77-1.67 (m, 1H), 1.38-1.29 (m, 1H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 144.0, 136.7, 135.3, 133.1, 130.7, 129.8, 128.5, 128.4, 127.9, 127.9, 82.7, 51.3, 37.1, 21.5, 20.0 ppm.

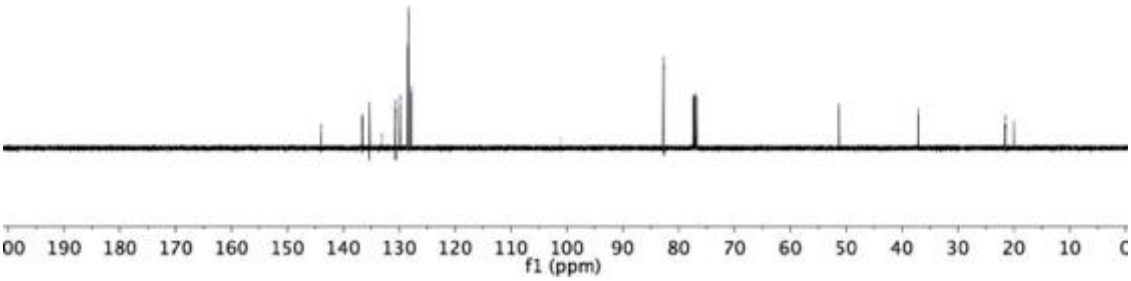
MP: 215 - 218 °C.

HRMS: (ESI) Calculated for $C_{30}H_{29}NO_4S$ [M+Na^+] = 522.17100, Found 522.17120.

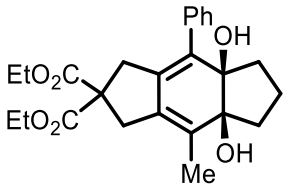
FTIR: (neat): 3456, 3021, 3051, 2968, 1597, 1346 cm^{-1}.


2.01
4.00
3.97
2.04
1.96
2.00
2.00
3.00
2.00
2.00
1.98
1.08
1.11
f1 (ppm)


143.96
136.66
135.33
133.10
130.68
129.76
128.46
128.35
127.86
127.86
127.85
101.06
82.68
77.23
51.29
37.10
21.53
19.96


f1 (ppm)

Diethyl (4a*S*,7a*R*)-4a,7a-dihydroxy-4-methyl-8-phenyl-3,4a,5,6,7,7a-hexahydro-*s*-indacene-2,2(1*H*)-dicarboxylate (4.3m)



The reaction was conducted with diyne **4.2e** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3m** (93.4 mg, 0.22 mmol) in 73% yield as a yellow solid.

TLC (SiO_2): R_f = 0.19 (hexanes : ethyl acetate = 3:1).

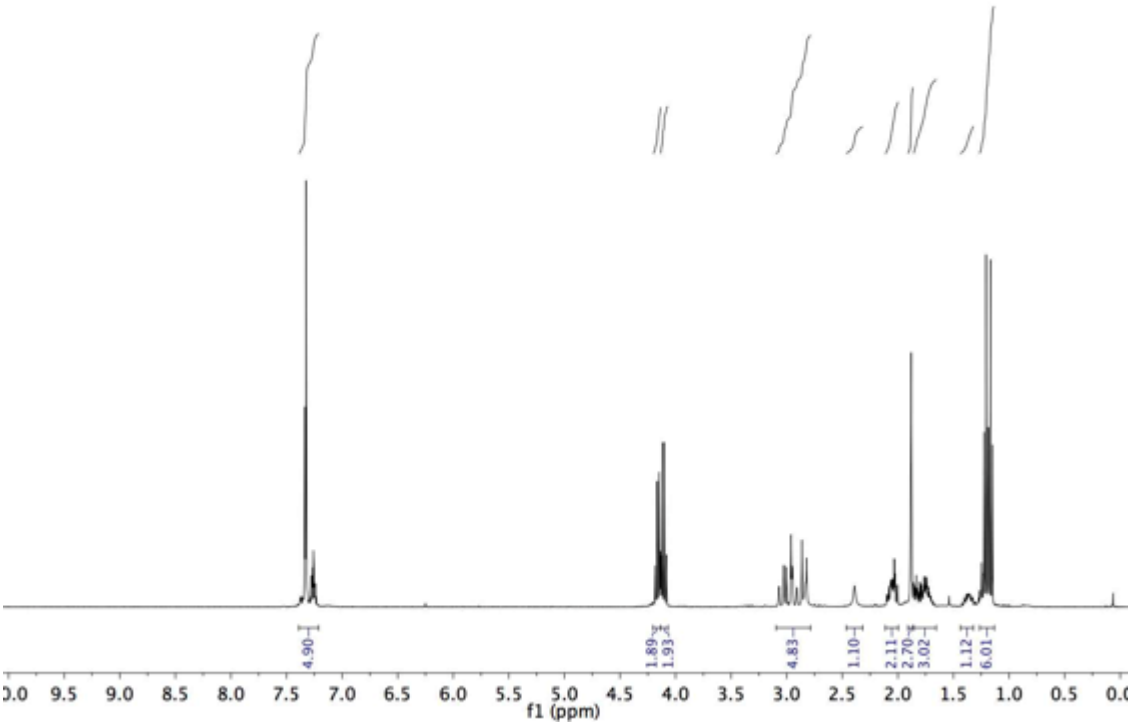
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.36-7.23 (m, 5H), 4.16 (q, *J* = 7.4 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.10- 2.81 (m, 5H), 2.40 (br, 1H), 2.11-2.01 (m, 2H), 1.89 (s, 3H), 1.88-1.68 (m, 3H), 1.42-1.32 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm.

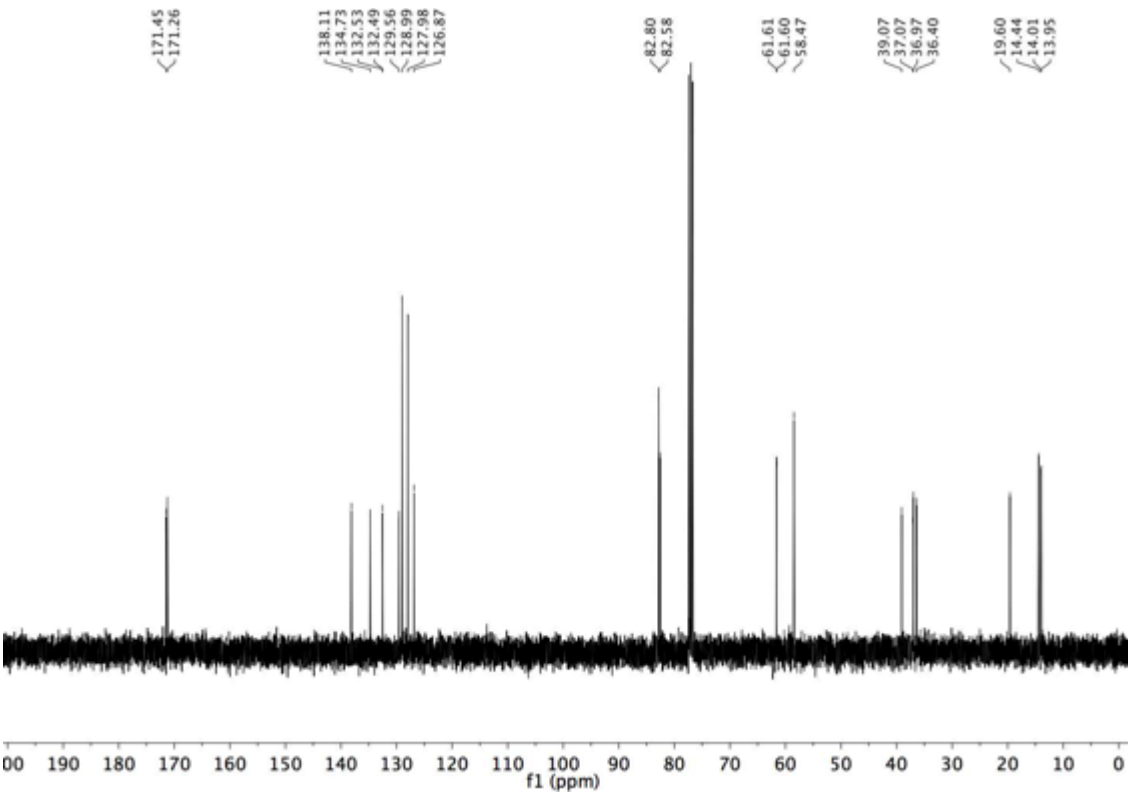
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.5, 171.3, 138.1, 134.7, 132.5, 132.5, 129.6, 129.0, 128.0, 126.9, 82.8, 82.6, 61.6, 61.6, 39.1, 37.1, 37.0, 36.4, 19.6, 14.4, 14.0, 14.0 ppm.

MP: 100 - 101 °C.

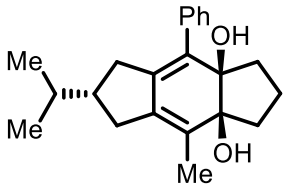
HRMS: (ESI) Calculated for $C_{25}H_{30}O_6$ [M+Na^+] = 449.19350, Found 449.1941.

FTIR: (neat): 3338, 2977, 1731 cm^{-1}.


4.90
1.89
1.93
4.83
1.10
2.11
2.70
3.02
1.12
6.01
f1 (ppm)


171.45
171.26
138.11
134.73
132.53
132.49
129.56
128.99
127.98
126.87
82.80
82.58
61.61
61.60
58.47
39.07
37.07
36.97
36.40
19.60
14.44
14.01
13.95
f1 (ppm)

(3a*S*,6*S*,8a*R*)-6-Isopropyl-4-methyl-8-phenyl-2,3,6,7-tetrahydro-*s*-indacene-3a,8a(1*H*,5*H*)-diol (4.3n)



The reaction was conducted at 120 ˚C for a 24 hour with diyne **4.2f** period in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 85:15) provided the title compound **4.3n** (59.4 mg, 0.18 mmol, dr = 1.6:1) in 61% yield as a yellow oil. (NOTE: Tentative relative configuration is provided.)

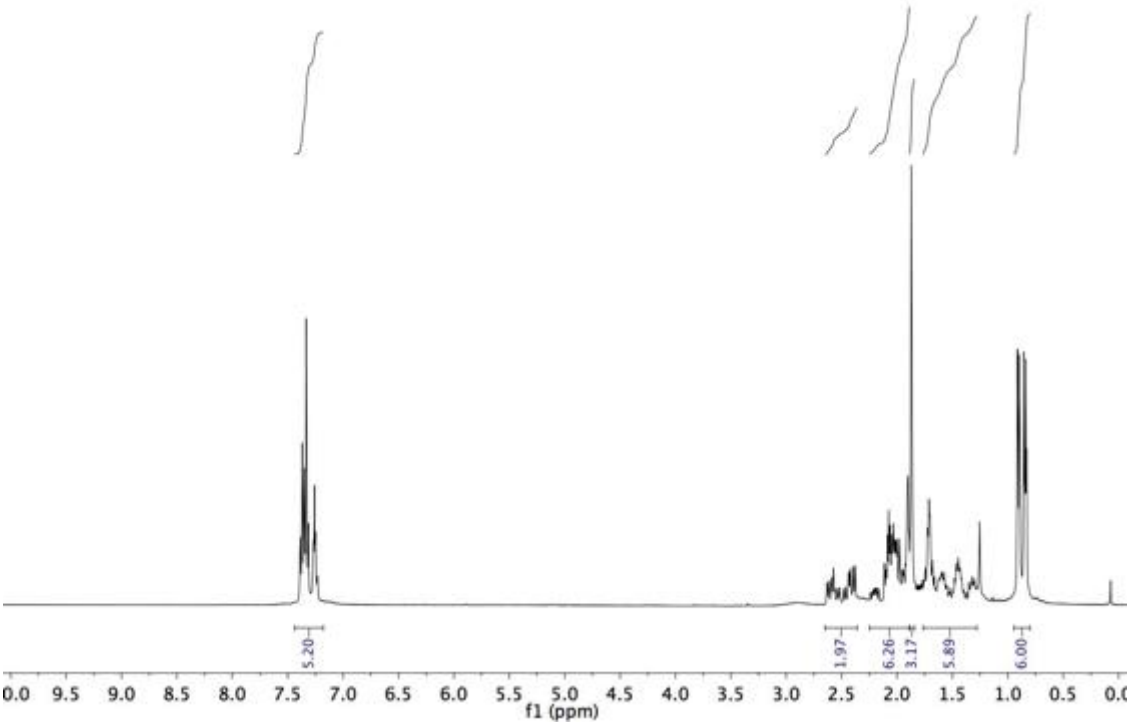
TLC (SiO_2): R_f = 0.50 (hexanes : ethyl acetate = 3:1).

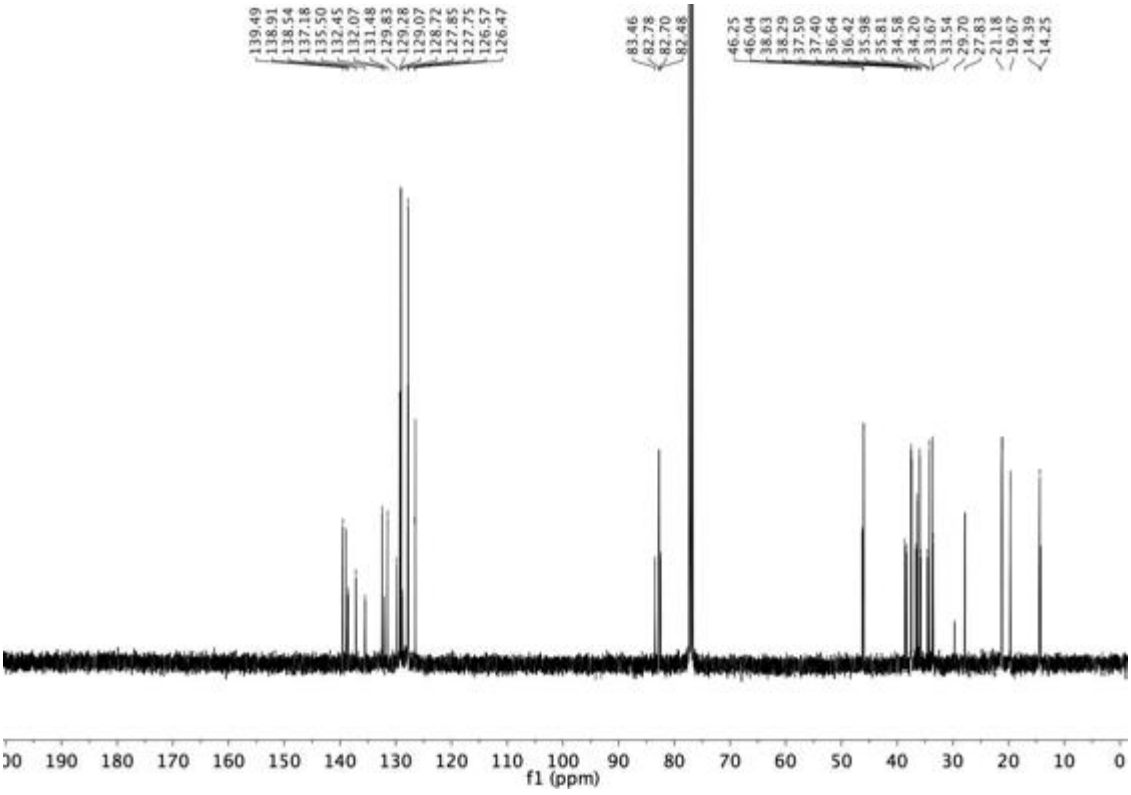
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.41-7.22 (m, 5H), 2.65-2.35 (m, 2H), 2.25-1.90 (m, 6H), 1.89 (s, 3H), 1.75-1.29 (m, 6H), 0.95-0.80 (m, 6H) ppm. (Note: Due to overlapping peaks integration values of diastereomers are reported together)

^{13}C NMR of the diastereomers: (100 MHz, $CDCl_3$): δ = 139.5, 138.9, 138.5, 137.2, 135.5, 132.5, 132.1, 131.5, 129.8, 129.3, 129.1, 128.7, 127.9, 127.8, 126.6, 126.5, 83.5, 82.8, 82.7, 82.5, 46.3, 46.0, 38.6, 38.3, 37.5, 37.4, 36.6, 36.4, 36.0, 35.8, 34.6, 34.2, 33.7, 33.5, 29.7, 27.8, 21.2, 19.7, 14.4, 14.3 ppm.

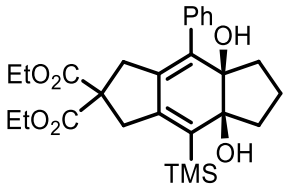
HRMS: (ESI) Calculated for $C_{22}H_{28}O_2$ [M+Na^+] = 347.1982, Found 347.1996.

FTIR: (neat): 3337, 2964, 2906 cm^{-1}.


5.20
1.97
6.26
3.17
5.89
6.00
f1 (ppm)


139.49
138.91
138.54
137.18
135.50
132.45
132.07
131.48
129.83
129.28
129.07
128.72
127.85
127.75
126.57
126.47
83.46
82.78
82.70
82.48
46.25
46.04
38.63
38.29
37.50
37.40
36.64
36.42
35.98
35.81
34.58
34.20
33.67
31.54
29.70
27.83
21.18
19.67
14.39
14.25
f1 (ppm)

Diethyl (4a*R*,7a*R*)-4a,7a-dihydroxy-4-phenyl-8-(trimethylsilyl)-3,4a,5,6,7,7a-hexahydro-*s*-indacene-2,2(1*H*)-dicarboxylate (4.3o)



The reaction was conducted for a 24 hour period with diyne **4.2g** in accordance with the general procedure. Flash column chromatography (SiO_2, DCM:Et_2O = 97:3) provided the title compound **4.3o** (97.8 mg, 0.20 mmol) in 67% yield as a yellow oil.

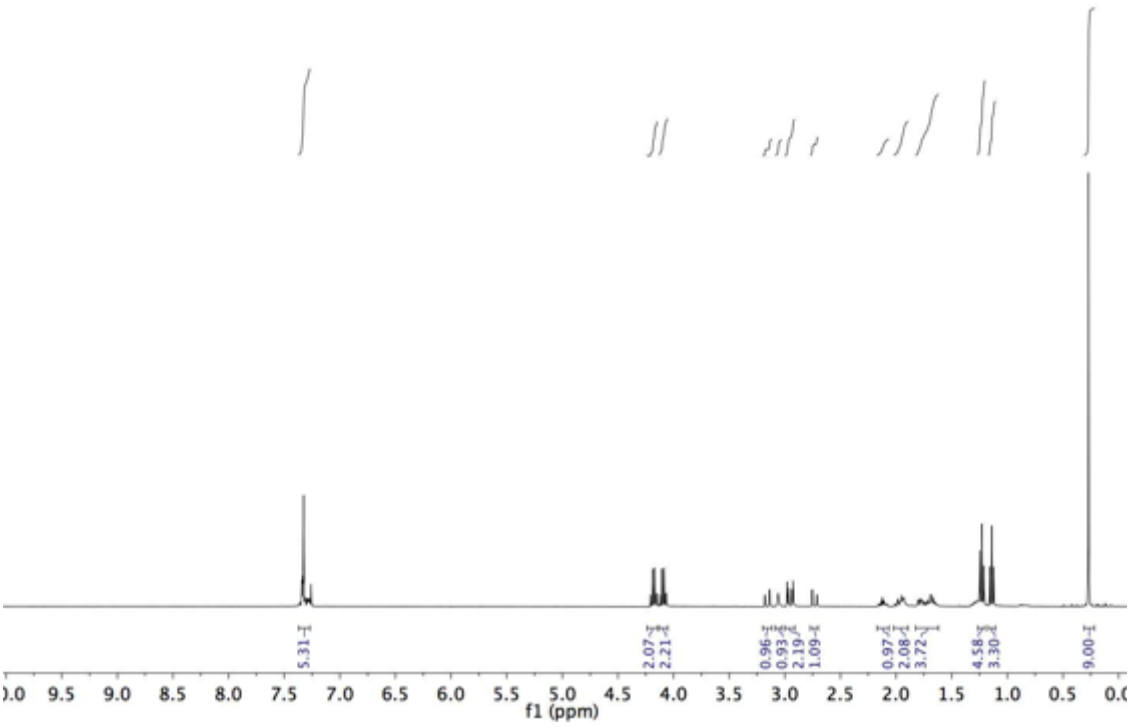
TLC (SiO_2): R_f = 0.65 (DCM : Et_2O = 10:1).

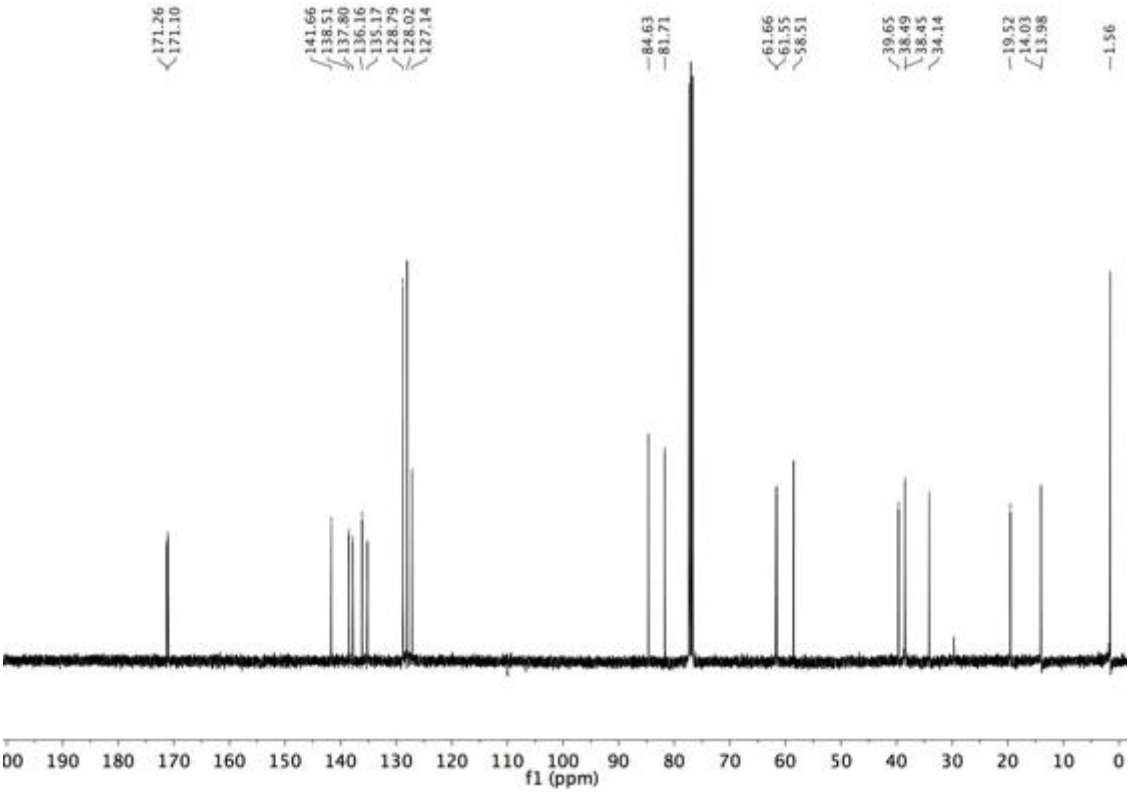
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.37-7.27 (m, 5H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.16 (d, *J* = 16.8 Hz, 1H), 3.06 (brs, 1H), 2.95 (dd, *J* = 16.6, *J* = 5.1 Hz, 2H), 2.73 (d, *J* = 16.8 Hz, 1H), 2,17-2.08 (m, 1H), 2.02-1.90 (m, 2H), 1.82-1.63 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 9H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.3, 171.1, 141.7, 138.5, 137.8, 136.2, 135.2, 128.8, 128.0, 127.1, 84.6, 81,7, 61.7, 61.6, 58.5, 39.7, 38.5, 38.5, 34.1, 19.5, 14.0, 14.0, 1.6 ppm.

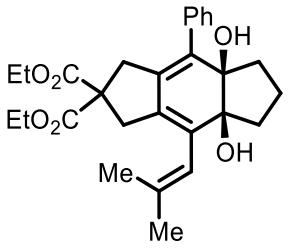
HRMS: (ESI) Calculated for $C_{27}H_{36}O_6$ [M+Na^+] = 507.21730, Found507.2181.

FTIR: (neat): 2980, 2945, 1728 cm^{-1}.


5.31
2.07
2.21
0.96
0.93
2.19
1.09
0.97
2.08
3.72
4.58
3.30
9.00
f1 (ppm)


171.26
171.10
141.66
138.51
137.80
136.16
135.17
128.79
128.02
127.14
84.63
81.71
61.66
61.55
58.51
39.65
38.49
38.45
34.14
19.52
14.03
13.98
1.56
f1 (ppm)

Diethyl (4a*S*,7a*R*)-4a,7a-dihydroxy-4-(2-methylprop-1-en-1-yl)-8-phenyl-3,4a,5,6,7,7a-hexahydro-*s*-indacene-2,2(1*H*)-dicarboxylate (4.3p)



The reaction was conducted with diyne **4.2h** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 80:20) provided the title compound **4.3p** (117.6 mg, 0.25 mmol) in 84% yield as a yellow oil.

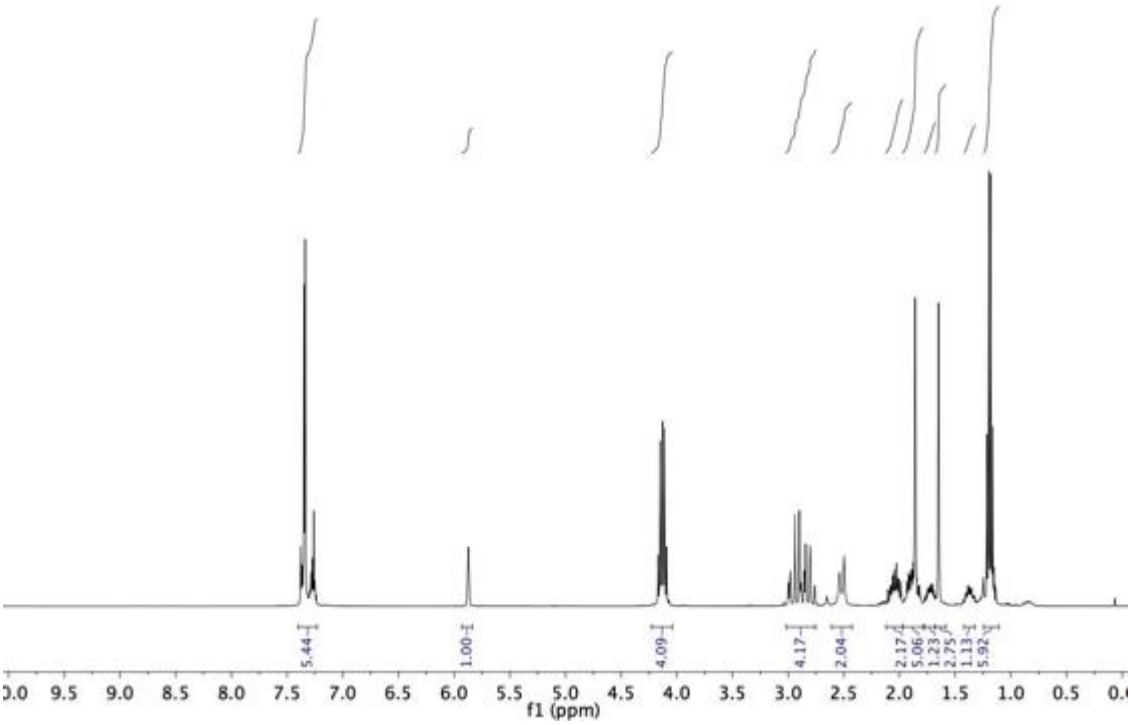
TLC (SiO_2): R_f = 0.25 (hexanes : ethyl acetate = 3:1).

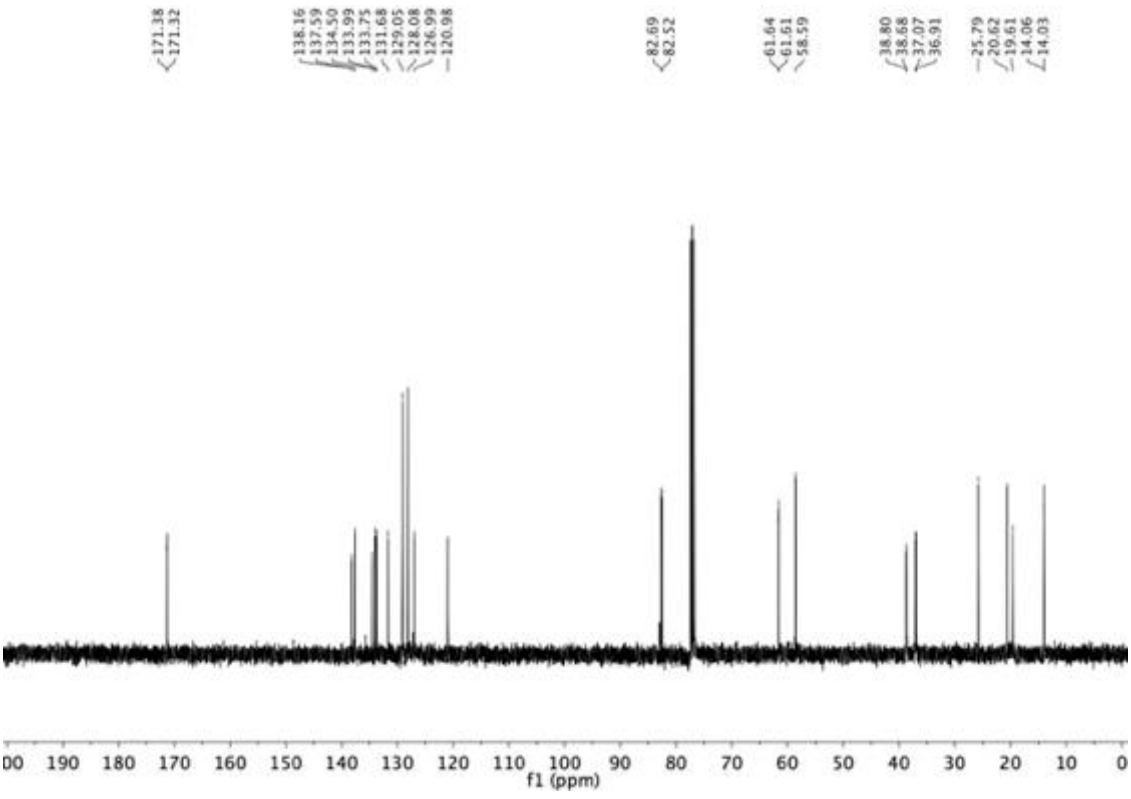
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.38-7.23 (m, 5H), 5.87 (s, 1H), 4.13 (q, *J* = 7.0 Hz, 2H*)* 4.12 (q, *J* = 7.0 Hz, 2H), , 3.00-2.75 (m, 4H), 2.58-2.48 (m, 2H), 2.11-1.98 (m, 2H), 1.94-1.80 (m, 2H), 1.86 (d, *J* = 1.5 Hz, 2H), 1.78-1.68 (m, 1H), 1.65 (d, *J* = 1.4 Hz, 2H), 1.43-1.31 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 171.4, 171.3, 138.2, 137.6, 134.5, 134.0, 133.8, 131.7, 129.1, 128.1, 127.0, 121.0, 82.7, 82.5 ppm.

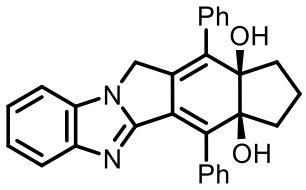
HRMS: (ESI) Calculated for $C_{28}H_{34}O_6S$ [M+Na^+] =489.22480, Found 489.2263.

FTIR: (neat): 2976, 1723 cm^{-1}.


5.44
1.00
4.09
4.17
2.04
2.17
5.06
1.23
2.75
1.13
5.92
f1 (ppm)


171.38
171.32
138.16
137.59
134.50
133.99
133.75
131.68
129.05
128.08
126.99
120.98
82.69
82.52
61.64
61.61
58.59
38.80
38.68
37.07
36.91
25.79
20.62
19.61
14.06
14.03
f1 (ppm)

(3a*S*,12a*R*)-4,12-Diphenyl-2,3-dihydrobenzo[4,5]imidazo[2,1-*a*]cyclopenta[*f*]isoindole-3a,12a(1*H*,11*H*)-diol (4.3q)



The reaction was conducted with diyne **4.2i** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 20:80 to 40:60 with 0.1% NEt_3) provided the title compound **4.3q** (83.4 mg, 0.19 mmol) in 64% yield as a white solid.

TLC (SiO_2): R_f = 0.60 (hexanes : ethyl acetate = 1:1).

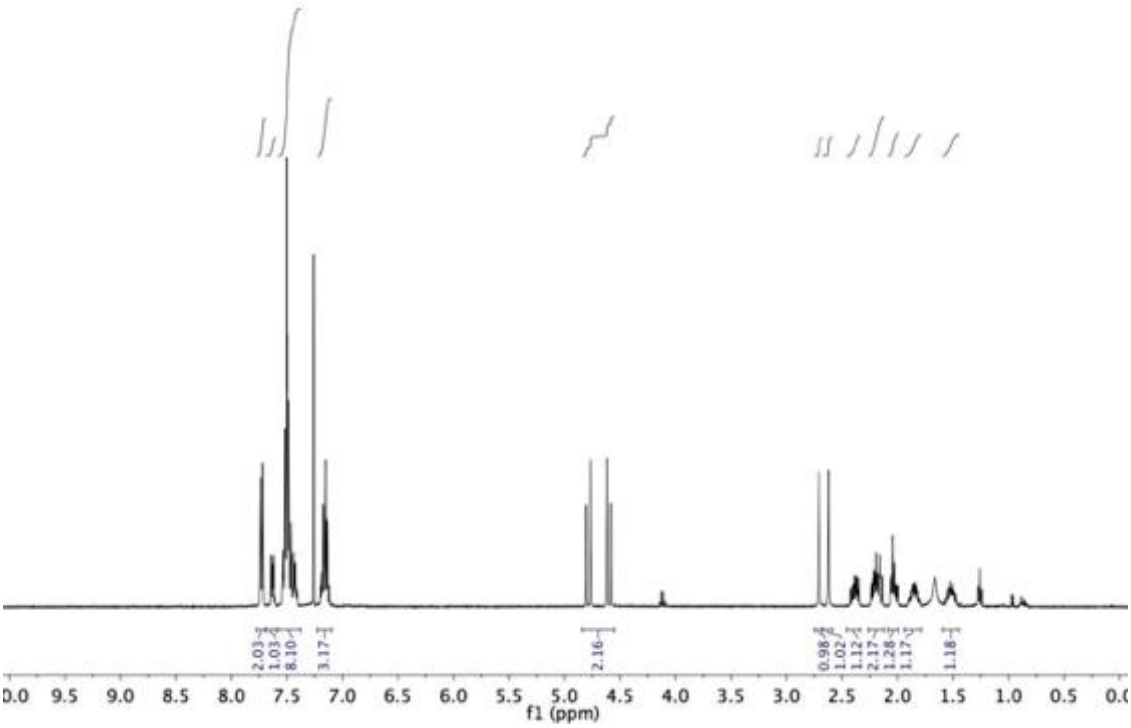
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.74-7.72 (m, 2H), 7.64-7.62 (m, 1H), 7.55-7.40 (m, 10H), 7.26-7.10 (m, 3H), 4.79 (d, *J* = 15.3 Hz, 1H), 4.60 (d, *J* = 15.3 Hz, 1H), 2.71 (s, 1H), 2.62 (s, 1H), 2.42-2.35 (m, 1H), 2.24-2.18 (m, 2H), 2.06-2.00 (m, 1H), 1.90-1.80 (m, 1H), 1.66-1.48 (m, 1H) ppm.

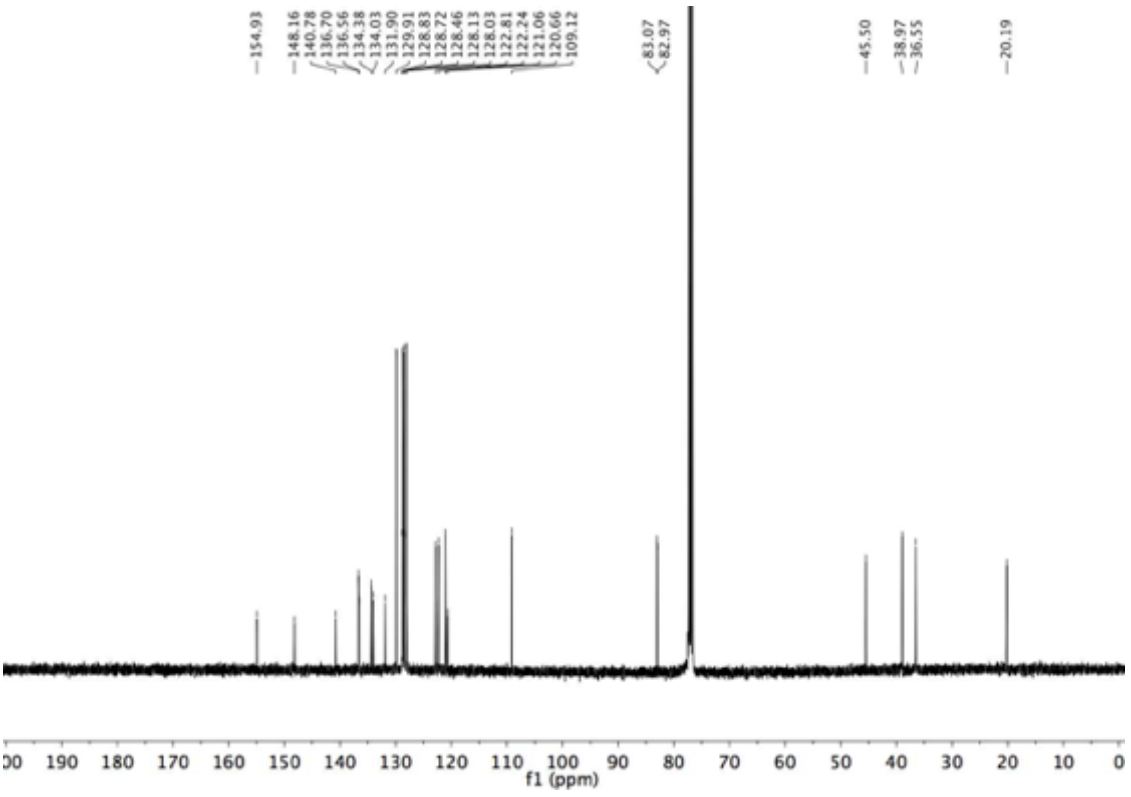
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 154.9, 148.2, 140.8, 136.7, 136.6, 134.4, 134.0, 131.9, 129.9, 128.8, 128.7, 128.5, 128.1, 128.0, 122.8, 122.2, 121.1, 120.7, 109.1, 83.1, 83.0, 45.5, 39.0, 36.6, 20.2 ppm.

MP: 193 – 196 ˚C.

HRMS: (ESI) Calculated for $C_{29}H_{24}N_2O_2$ [M+H$^+$] =433.19110, Found433.19220.

FTIR: (neat): 2923, 2953 cm^{-1}.


2.03
1.03
8.10
3.17
2.16
0.98
1.02
1.12
2.17
1.28
1.17
1.18
f1 (ppm)


154.93
148.16
140.78
136.70
136.56
134.38
134.03
131.90
129.91
128.83
128.72
128.46
128.13
128.03
122.81
122.24
121.06
120.66
109.12
83.07
82.97
45.50
38.97
36.55
20.19
f1 (ppm)

Procedure for Redox-Level Independent Cycloaddition Reaction

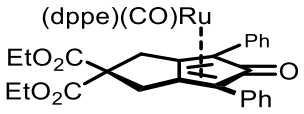
From *dehydro*-**4.1f**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), $AdCO_2H$ (3.2 mg, 0.018 mmol, 6 mol%), *dehydro*-**4.1f** (55.3 mg, 0.3 mmol, 100 mol%) and **4.2a** (116.6 mg, 0.3 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.5 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 14 hours. After cooling to room temperature, the mixture was concentrated *in vacuo*. Flash column chromatography (SiO_2: hexanes:ethyl acetate = 80:20) provided **4.3f** (137.4 mg, 0.24 mmol) in 80% yield as a pale yellow solid.

From *didehydro*-**4.1f**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), $AdCO_2H$ (3.2 mg, 0.018 mmol, 6 mol%), *didehydro*-**4.1f** (54.7 mg, 0.3 mmol, 100 mol%), **4.2a** (116.6 mg, 0.3 mmol, 100 mol%) and *i*-PrOH (68.8 μL, 0.9 mmol, 300 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.6 mL, 0.5 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 14 hours. After cooling to room temperature, the mixture was concentrated *in vacuo*. Flash column chromatography (SiO_2: hexanes:ethyl acetate = 80:20) provided **4.3f** (128.9 mg, 0.23 mmol) in 75% yield as a pale yellow solid.

Preparation of Ru-Complex II



A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (32.0 mg, 0.05 mmol, 33 mol%), **4.2a** (58 mg, 0.15 mmol, 100 mol%), dppe (59.8 mg, 0.15 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and THF (0.10 mL, 1.5 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 16 hours. After cooling to room temperature, the formed precipitate was filtered off, washed with cold THF (0.3 ml) and dried under high vacuum to give the title compound (77.0 mg, 0.08 mmol) in 55% yield as a yellow solid.

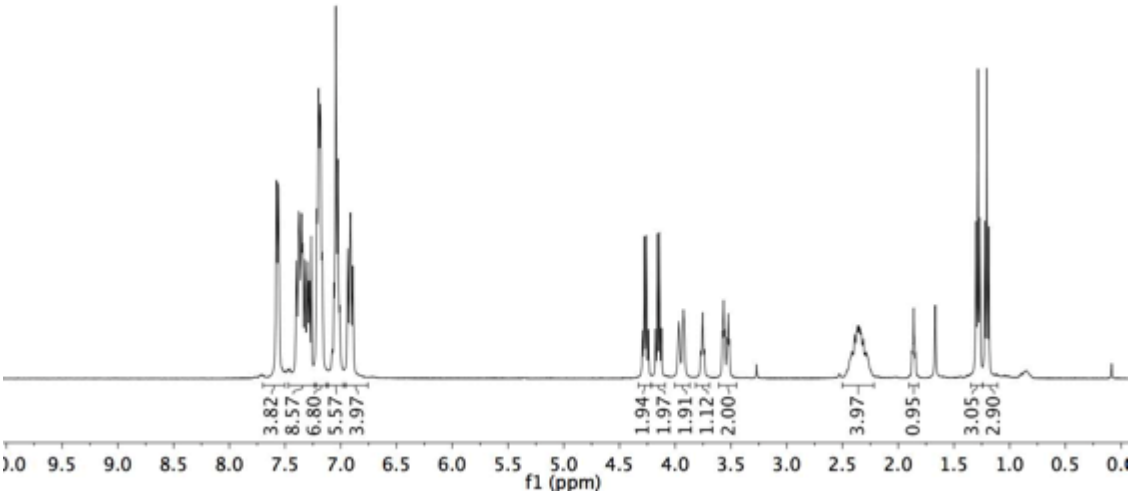
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.58-7.56 (m, 4H), 7.40-7.28 (m, 9H), 7.22-7.17 (m, 7H), 7.08-7.01 (m, 6H), 6.92 (dt, *J* = 10.6 Hz, *J* = 7.6 Hz, 4H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.95 (dt, *J* = 16.5 Hz, *J* = 3.5 Hz, 2H), 3.56 (dt, *J* = 16.5 Hz, *J* = 4.3 Hz, 2H), 2.46-2.25 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm.

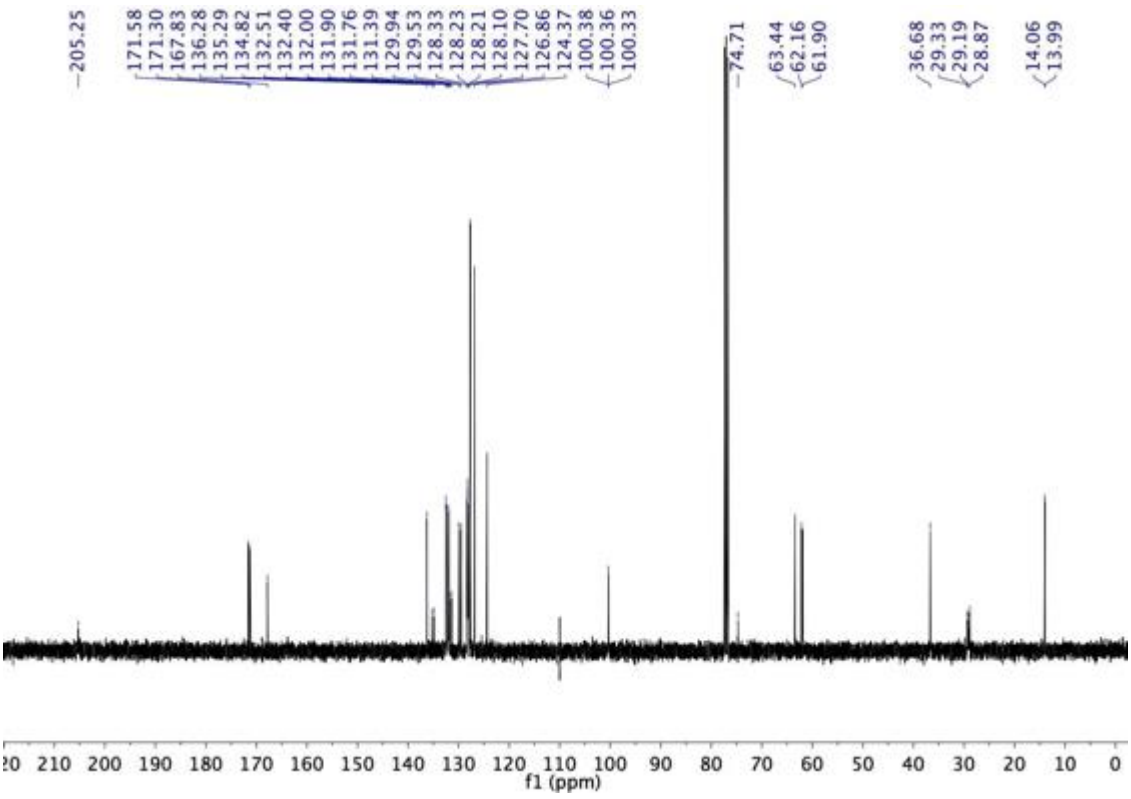
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 205.3, 171.6, 171.3, 167.8, 136.3, 135.3, 134.8, 132.5 (m, PPh_2), 132.0 (m, PPh_2), 131.8, 131.4, 129.9, 129.5 (s, PPh_2), 128.3 (m, PPh_2), 127.7, 126.9, 124.4, 100.4, 74.7, 63.4, 62.2, 61.9, 36.7, 29.2 (m, CH_2PPh_2), 14.1, 14.0.

MP: 145 - 148 °C.

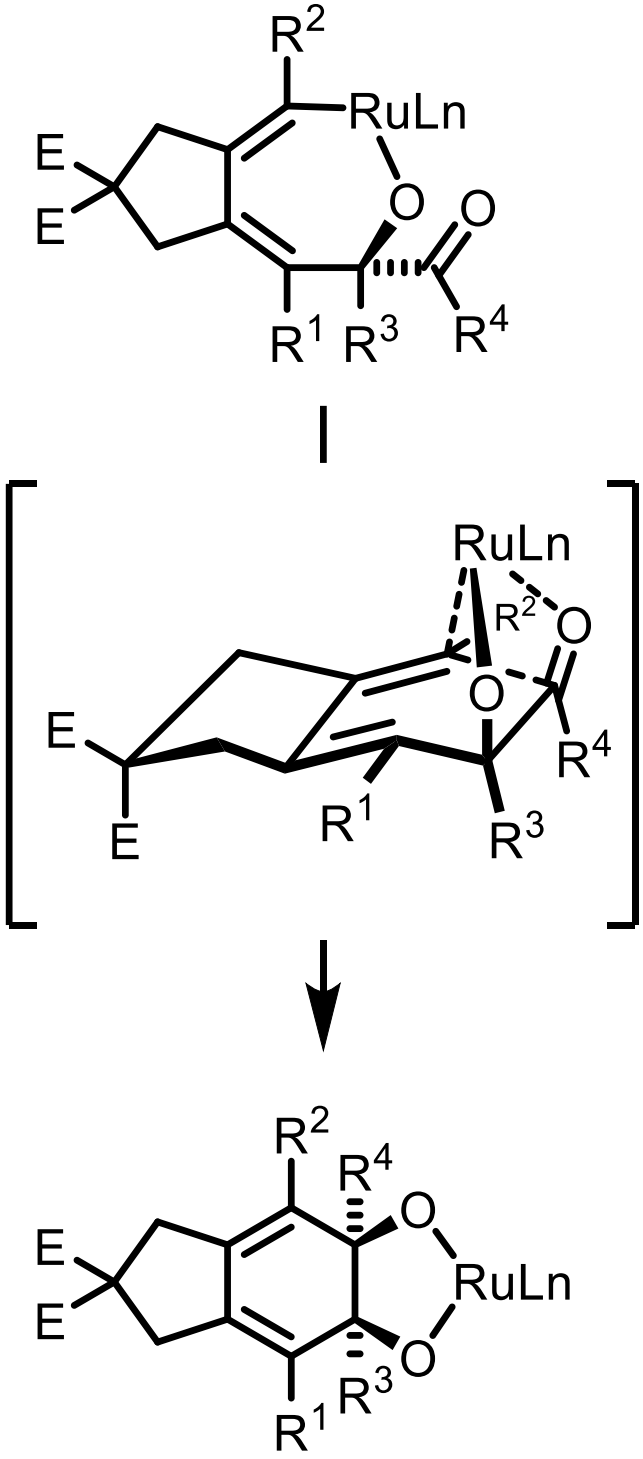
LRMS (ESI): 945.2[$M+H^+$].

FTIR: (neat): 3456, 3021, 3051, 2968, 1597, 1346 cm^{-1}.


3.82
8.57
6.80
5.57
3.97
1.94
1.97
1.91
1.12
2.00
3.97
0.95
3.05
2.90
f1 (ppm)


205.25
171.58
171.30
167.83
136.28
135.29
134.82
132.51
132.40
132.00
131.90
131.76
131.39
129.94
129.53
128.33
128.23
128.21
128.10
127.70
126.86
124.37
100.38
100.36
100.33
74.71
63.44
62.16
61.90
36.68
29.33
29.19
28.87
14.06
13.99
f1 (ppm)

Model Accounting for syn-Diastereoselectivity



Single Crystal Diffraction Data

X-ray Experimental for complex **4.3a**-$CHCl_3$:

Crystals grew as colorless prisms by slow evaporation from $CHCl_3$. The data crystal was cut from a larger crystal and had approximate dimensions; 0.25 x 0.18 x 0.14 mm. The data were collected on a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD using a graphite monochromator with MoKα radiation (γ = 0.71073Å). A total of 1080 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 24 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[17] The structure was solved by direct methods using SIR20042 and refined by full-matrix least-squares on F^{16} with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[18] Structure analysis was aided by use of the programs PLATON98[19] and WinGX.[20] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to oxygen were located in a ΔF map and refined with isotropic displacement parameters.

The ethyl group on one ethyl ester portion of molecule **4.3a** was disordered. The disorder was modeled by assigning the variable x to the site occupancy factors to C59 and C60, while (1-x) was assigned to the site occupancy factors for C59a and C60a. The geometry of the two pairs of atoms was restrained to be equivalent throughout the refinement process. A common isotropic displacement parameter was refined for the four atoms while refining the variable x. The major component of the disorder refined to a site occupancy of 81(2)%.

The function, $\sum w(|Fo|^2 - |Fc|^2)$,15 was minimized, where $w = 1/[(\sum (Fo))^2 + (0.0475*P)^2 + (1.3113*P)]$ and $P = (|Fo|^2 + {}^2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.127, with R(F) equal to 0.0521 and a goodness of fit, S, = 1.04. Definitions used for calculating R(F), $Rw(F^2)$ and the goodness of fit, S, are given below.[22] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[23] All figures were generated using SHELXTL/PC.[24] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 4.3. Crystal data and structure refinement for **4.3a**.

Empirical formula	C30 H32 O6	
Formula weight	488.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.0712(18) Å	a= 81.460(3)°.
	b = 13.679(2) Å	b= 84.332(4)°.
	c = 15.741(2) Å	g = 73.752(3)°.
Volume	2463.2(6) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	1040	
Crystal size	0.250 x 0.180 x 0.140 mm^3	
Theta range for data collection	2.998 to 27.481°.	
Index ranges	-15<=h<=15, -17<=k<=17, -20<=l<=20	
Reflections collected	51448	
Independent reflections	11248 [R(int) = 0.0620]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.771	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11248 / 32 / 680	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1170	
R indices (all data)	R1 = 0.0730, wR2 = 0.1268	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.365 and -0.234 $e.Å^{-3}$	

Table 4.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4.3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	1658(1)	5857(1)	7752(1)	16(1)
C2	2838(1)	5264(1)	8135(1)	17(1)
C3	3406(1)	4472(1)	7525(1)	15(1)
C4	4394(1)	3708(1)	7597(1)	15(1)
C5	4830(1)	3124(1)	6819(1)	15(1)
C6	5619(1)	3643(1)	6173(1)	18(1)
C7	5395(2)	3480(1)	5260(1)	20(1)
C8	4572(1)	2790(1)	5406(1)	16(1)
C9	3866(1)	3070(1)	6242(1)	16(1)
C10	2953(1)	4108(1)	6118(1)	14(1)
C11	2762(1)	4727(1)	6737(1)	15(1)
C12	1864(1)	5748(1)	6774(1)	16(1)
C13	5129(1)	3512(1)	8346(1)	16(1)
C14	4658(2)	3413(1)	9193(1)	20(1)
C15	5320(2)	3311(1)	9894(1)	24(1)
C16	6482(2)	3298(1)	9762(1)	25(1)
C17	6974(2)	3366(1)	8924(1)	23(1)
C18	6312(1)	3462(1)	8225(1)	19(1)
C19	2263(1)	4387(1)	5339(1)	16(1)
C20	1739(2)	3700(1)	5069(1)	21(1)
C21	1075(2)	3990(1)	4355(1)	26(1)
C22	929(2)	4962(1)	3893(1)	26(1)
C23	1457(2)	5649(1)	4143(1)	22(1)
C24	2116(1)	5358(1)	4861(1)	18(1)
C25	751(1)	5308(1)	8138(1)	17(1)
C26	-913(2)	5298(1)	9053(1)	29(1)
C27	-1823(2)	6042(2)	9541(1)	35(1)
C28	1268(1)	6969(1)	7936(1)	16(1)
C29	-119(2)	8575(1)	7576(1)	23(1)
C30	-1153(2)	8571(1)	8190(1)	28(1)
C31	3562(1)	-1090(1)	7176(1)	17(1)

C32	3284(1)	-965(1)	8144(1)	17(1)
C33	2385(1)	59(1)	8139(1)	15(1)
C34	2171(1)	717(1)	8727(1)	15(1)
C35	1284(1)	1753(1)	8524(1)	15(1)
C36	575(1)	2154(1)	9324(1)	16(1)
C37	-249(2)	1470(1)	9553(1)	19(1)
C38	-459(1)	1173(1)	8676(1)	17(1)
C39	318(1)	1640(1)	7984(1)	15(1)
C40	776(1)	1011(1)	7238(1)	15(1)
C41	1783(1)	275(1)	7334(1)	16(1)
C42	2416(1)	-514(1)	6740(1)	18(1)
C43	2804(1)	502(1)	9529(1)	15(1)
C44	2898(1)	-426(1)	10070(1)	17(1)
C45	3493(1)	-637(1)	10819(1)	20(1)
C46	3998(1)	81(1)	11041(1)	22(1)
C47	3906(2)	1004(1)	10510(1)	22(1)
C48	3316(1)	1219(1)	9762(1)	19(1)
C49	62(1)	1216(1)	6478(1)	16(1)
C50	-1121(1)	1258(1)	6587(1)	20(1)
C51	-1800(2)	1459(1)	5884(1)	23(1)
C52	-1313(2)	1638(1)	5053(1)	25(1)
C53	-146(2)	1607(1)	4934(1)	25(1)
C54	536(2)	1391(1)	5638(1)	20(1)
C55	4520(1)	-584(1)	6813(1)	17(1)
C56	6016(2)	-582(2)	5707(1)	27(1)
C57	7076(2)	-1089(2)	6204(1)	35(1)
C58	3966(1)	-2219(1)	7041(1)	18(1)
C59	5589(2)	-3697(2)	7208(2)	22(1)
C60	6691(2)	-4009(2)	7663(2)	30(1)
C59A	5353(9)	-3836(10)	7542(8)	29(3)
C60A	6540(10)	-3911(10)	7128(9)	44(3)
O1	5490(1)	2091(1)	7091(1)	18(1)
O2	3349(1)	2252(1)	6560(1)	20(1)
O3	732(1)	4484(1)	7954(1)	28(1)
O4	-11(1)	5803(1)	8702(1)	27(1)
O5	1623(1)	7299(1)	8493(1)	24(1)

O6	462(1)	7527(1)	7397(1)	20(1)
O7	1921(1)	2443(1)	8073(1)	19(1)
O8	-364(1)	2654(1)	7675(1)	19(1)
O9	4774(1)	66(1)	7130(1)	24(1)
O10	5030(1)	-949(1)	6081(1)	24(1)
O11	3476(1)	-2658(1)	6660(1)	24(1)
O12	4961(1)	-2670(1)	7423(1)	29(1)

Table 4.5. Bond lengths [Å] and angles [°] for **4.3a**.

C1-C25	1.525(2)	C15-C16	1.393(3)
C1-C28	1.524(2)	C15-H15	0.95
C1-C12	1.557(2)	C16-C17	1.394(3)
C1-C2	1.559(2)	C16-H16	0.95
C2-C3	1.527(2)	C17-C18	1.391(2)
C2-H2A	0.99	C17-H17	0.95
C2-H2B	0.99	C18-H18	0.95
C3-C4	1.350(2)	C19-C20	1.402(2)
C3-C11	1.475(2)	C19-C24	1.401(2)
C4-C13	1.493(2)	C20-C21	1.390(2)
C4-C5	1.530(2)	C20-H20	0.95
C5-O1	1.4392(19)	C21-C22	1.391(3)
C5-C6	1.555(2)	C21-H21	0.95
C5-C9	1.569(2)	C22-C23	1.391(3)
C6-C7	1.548(2)	C22-H22	0.95
C6-H6A	0.99	C23-C24	1.391(2)
C6-H6B	0.99	C23-H23	0.95
C7-C8	1.531(2)	C24-H24	0.95
C7-H7A	0.99	C25-O3	1.211(2)
C7-H7B	0.99	C25-O4	1.327(2)
C8-C9	1.534(2)	C26-O4	1.469(2)
C8-H8A	0.99	C26-C27	1.508(3)
C8-H8B	0.99	C26-H26A	0.99
C9-O2	1.4328(19)	C26-H26B	0.99
C9-C10	1.534(2)	C27-H27A	0.98
C10-C11	1.346(2)	C27-H27B	0.98
C10-C19	1.493(2)	C27-H27C	0.98
C11-C12	1.514(2)	C28-O5	1.206(2)
C12-H12A	0.99	C28-O6	1.343(2)
C12-H12B	0.99	C29-O6	1.4639(19)
C13-C14	1.400(2)	C29-C30	1.503(2)
C13-C18	1.406(2)	C29-H29A	0.99
C14-C15	1.393(2)	C29-H29B	0.99
C14-H14	0.95	C30-H30A	0.98

C30-H30B	0.98	C45-C46	1.392(2)
C30-H30C	0.98	C45-H45	0.95
C31-C58	1.524(2)	C46-C47	1.391(3)
C31-C55	1.530(2)	C46-H46	0.95
C31-C32	1.553(2)	C47-C48	1.387(2)
C31-C42	1.557(2)	C47-H47	0.95
C32-C33	1.513(2)	C48-H48	0.95
C32-H32A	0.99	C49-C54	1.402(2)
C32-H32B	0.99	C49-C50	1.406(2)
C33-C34	1.343(2)	C50-C51	1.392(2)
C33-C41	1.474(2)	C50-H50	0.95
C34-C43	1.490(2)	C51-C52	1.396(3)
C34-C35	1.530(2)	C51-H51	0.95
C35-O7	1.4428(19)	C52-C53	1.392(3)
C35-C36	1.534(2)	C52-H52	0.95
C35-C39	1.563(2)	C53-C54	1.394(2)
C36-C37	1.531(2)	C53-H53	0.95
C36-H36A	0.99	C54-H54	0.95
C36-H36B	0.99	C55-O9	1.203(2)
C37-C38	1.558(2)	C55-O10	1.347(2)
C37-H37A	0.99	C56-O10	1.457(2)
C37-H37B	0.99	C56-C57	1.506(3)
C38-C39	1.550(2)	C56-H56A	0.99
C38-H38A	0.99	C56-H56B	0.99
C38-H38B	0.99	C57-H57A	0.98
C39-O8	1.4413(19)	C57-H57B	0.98
C39-C40	1.527(2)	C57-H57C	0.98
C40-C41	1.349(2)	C58-O11	1.203(2)
C40-C49	1.491(2)	C58-O12	1.343(2)
C41-C42	1.524(2)	C59-O12	1.469(2)
C42-H42A	0.99	C59-C60	1.497(3)
C42-H42B	0.99	C59-H59A	0.99
C43-C48	1.403(2)	C59-H59B	0.99
C43-C44	1.403(2)	C60-H60A	0.98
C44-C45	1.392(2)	C60-H60B	0.98
C44-H44	0.95	C60-H60C	0.98

C59A-C60A	1.497(9)	C60A-H60F	0.98
C59A-O12	1.521(13)	O1-H1O	0.85(3)
C59A-H59C	0.99	O2-H2O	0.83(2)
C59A-H59D	0.99	O7-H7O	0.79(2)
C60A-H60D	0.98	O8-H8O	0.81(3)
C60A-H60E	0.98		

C25-C1-C28	109.49(13)	H6A-C6-H6B	108.6
C25-C1-C12	108.76(13)	C8-C7-C6	104.97(13)
C28-C1-C12	113.32(13)	C8-C7-H7A	110.8
C25-C1-C2	108.51(13)	C6-C7-H7A	110.8
C28-C1-C2	112.30(13)	C8-C7-H7B	110.8
C12-C1-C2	104.25(12)	C6-C7-H7B	110.8
C3-C2-C1	104.93(13)	H7A-C7-H7B	108.8
C3-C2-H2A	110.8	C7-C8-C9	104.46(13)
C1-C2-H2A	110.8	C7-C8-H8A	110.9
C3-C2-H2B	110.8	C9-C8-H8A	110.9
C1-C2-H2B	110.8	C7-C8-H8B	110.9
H2A-C2-H2B	108.8	C9-C8-H8B	110.9
C4-C3-C11	121.67(14)	H8A-C8-H8B	108.9
C4-C3-C2	129.28(14)	O2-C9-C10	111.56(13)
C11-C3-C2	108.73(13)	O2-C9-C8	107.15(13)
C3-C4-C13	122.55(14)	C10-C9-C8	112.68(13)
C3-C4-C5	117.13(14)	O2-C9-C5	112.96(13)
C13-C4-C5	119.86(13)	C10-C9-C5	110.59(13)
O1-C5-C4	110.43(12)	C8-C9-C5	101.48(12)
O1-C5-C6	107.68(12)	C11-C10-C19	121.58(14)
C4-C5-C6	112.05(13)	C11-C10-C9	118.78(14)
O1-C5-C9	108.14(12)	C19-C10-C9	119.57(13)
C4-C5-C9	115.18(13)	C10-C11-C3	123.37(14)
C6-C5-C9	102.86(12)	C10-C11-C12	127.78(15)
C7-C6-C5	107.06(13)	C3-C11-C12	108.82(13)
C7-C6-H6A	110.3	C11-C12-C1	104.27(13)
C5-C6-H6A	110.3	C11-C12-H12A	110.9
C7-C6-H6B	110.3	C1-C12-H12A	110.9
C5-C6-H6B	110.3	C11-C12-H12B	110.9

C1-C12-H12B	110.9	C23-C24-H24	119.3
H12A-C12-H12B	108.9	C19-C24-H24	119.3
C14-C13-C18	117.54(15)	O3-C25-O4	122.70(16)
C14-C13-C4	121.35(15)	O3-C25-C1	122.99(15)
C18-C13-C4	121.06(14)	O4-C25-C1	114.32(14)
C15-C14-C13	121.55(16)	O4-C26-C27	107.89(15)
C15-C14-H14	119.2	O4-C26-H26A	110.1
C13-C14-H14	119.2	C27-C26-H26A	110.1
C16-C15-C14	120.14(16)	O4-C26-H26B	110.1
C16-C15-H15	119.9	C27-C26-H26B	110.1
C14-C15-H15	119.9	H26A-C26-H26B	108.4
C15-C16-C17	119.09(16)	C26-C27-H27A	109.5
C15-C16-H16	120.5	C26-C27-H27B	109.5
C17-C16-H16	120.5	H27A-C27-H27B	109.5
C18-C17-C16	120.66(16)	C26-C27-H27C	109.5
C18-C17-H17	119.7	H27A-C27-H27C	109.5
C16-C17-H17	119.7	H27B-C27-H27C	109.5
C17-C18-C13	120.95(16)	O5-C28-O6	124.80(15)
C17-C18-H18	119.5	O5-C28-C1	124.86(15)
C13-C18-H18	119.5	O6-C28-C1	110.33(13)
C20-C19-C24	118.21(15)	O6-C29-C30	109.78(14)
C20-C19-C10	121.69(15)	O6-C29-H29A	109.7
C24-C19-C10	120.09(14)	C30-C29-H29A	109.7
C21-C20-C19	120.46(16)	O6-C29-H29B	109.7
C21-C20-H20	119.8	C30-C29-H29B	109.7
C19-C20-H20	119.8	H29A-C29-H29B	108.2
C22-C21-C20	120.49(16)	C29-C30-H30A	109.5
C22-C21-H21	119.8	C29-C30-H30B	109.5
C20-C21-H21	119.8	H30A-C30-H30B	109.5
C21-C22-C23	119.91(16)	C29-C30-H30C	109.5
C21-C22-H22	120.0	H30A-C30-H30C	109.5
C23-C22-H22	120.0	H30B-C30-H30C	109.5
C22-C23-C24	119.47(16)	C58-C31-C55	108.33(13)
C22-C23-H23	120.3	C58-C31-C32	111.18(13)
C24-C23-H23	120.3	C55-C31-C32	110.08(13)
C23-C24-C19	121.45(16)	C58-C31-C42	112.57(13)

C55-C31-C42	110.01(13)	C37-C38-H38B	110.4
C32-C31-C42	104.65(13)	H38A-C38-H38B	108.6
C33-C32-C31	103.84(13)	O8-C39-C40	110.59(13)
C33-C32-H32A	111.0	O8-C39-C38	106.52(13)
C31-C32-H32A	111.0	C40-C39-C38	114.50(13)
C33-C32-H32B	111.0	O8-C39-C35	108.17(12)
C31-C32-H32B	111.0	C40-C39-C35	113.89(13)
H32A-C32-H32B	109.0	C38-C39-C35	102.57(12)
C34-C33-C41	123.29(14)	C41-C40-C49	124.64(14)
C34-C33-C32	128.07(15)	C41-C40-C39	117.04(14)
C41-C33-C32	108.56(13)	C49-C40-C39	118.26(13)
C33-C34-C43	122.86(14)	C40-C41-C33	121.30(14)
C33-C34-C35	117.44(14)	C40-C41-C42	129.47(15)
C43-C34-C35	119.61(13)	C33-C41-C42	108.93(13)
O7-C35-C34	106.31(12)	C41-C42-C31	104.71(13)
O7-C35-C36	113.13(13)	C41-C42-H42A	110.8
C34-C35-C36	113.04(13)	C31-C42-H42A	110.8
O7-C35-C39	112.61(12)	C41-C42-H42B	110.8
C34-C35-C39	110.56(12)	C31-C42-H42B	110.8
C36-C35-C39	101.31(12)	H42A-C42-H42B	108.9
C37-C36-C35	103.86(13)	C48-C43-C44	118.51(15)
C37-C36-H36A	111.0	C48-C43-C34	121.08(15)
C35-C36-H36A	111.0	C44-C43-C34	120.42(14)
C37-C36-H36B	111.0	C45-C44-C43	120.90(15)
C35-C36-H36B	111.0	C45-C44-H44	119.5
H36A-C36-H36B	109.0	C43-C44-H44	119.5
C36-C37-C38	104.94(13)	C44-C45-C46	119.91(16)
C36-C37-H37A	110.8	C44-C45-H45	120.0
C38-C37-H37A	110.8	C46-C45-H45	120.0
C36-C37-H37B	110.8	C47-C46-C45	119.60(16)
C38-C37-H37B	110.8	C47-C46-H46	120.2
H37A-C37-H37B	108.8	C45-C46-H46	120.2
C39-C38-C37	106.51(13)	C48-C47-C46	120.80(16)
C39-C38-H38A	110.4	C48-C47-H47	119.6
C37-C38-H38A	110.4	C46-C47-H47	119.6
C39-C38-H38B	110.4	C47-C48-C43	120.28(16)

C47-C48-H48	119.9	O11-C58-C31	126.11(15)
C43-C48-H48	119.9	O12-C58-C31	109.78(14)
C54-C49-C50	118.05(15)	O12-C59-C60	106.78(18)
C54-C49-C40	121.40(15)	O12-C59-H59A	110.4
C50-C49-C40	120.53(15)	C60-C59-H59A	110.4
C51-C50-C49	121.15(16)	O12-C59-H59B	110.4
C51-C50-H50	119.4	C60-C59-H59B	110.4
C49-C50-H50	119.4	H59A-C59-H59B	108.6
C50-C51-C52	119.95(17)	C59-C60-H60A	109.5
C50-C51-H51	120.0	C59-C60-H60B	109.5
C52-C51-H51	120.0	H60A-C60-H60B	109.5
C53-C52-C51	119.64(16)	C59-C60-H60C	109.5
C53-C52-H52	120.2	H60A-C60-H60C	109.5
C51-C52-H52	120.2	H60B-C60-H60C	109.5
C52-C53-C54	120.30(17)	C60A-C59A-O12	95.4(8)
C52-C53-H53	119.9	C60A-C59A-H59C	112.7
C54-C53-H53	119.9	O12-C59A-H59C	112.7
C53-C54-C49	120.91(16)	C60A-C59A-H59D	112.7
C53-C54-H54	119.5	O12-C59A-H59D	112.7
C49-C54-H54	119.5	H59C-C59A-H59D	110.2
O9-C55-O10	124.29(16)	C59A-C60A-H60D	109.5
O9-C55-C31	124.68(15)	C59A-C60A-H60E	109.5
O10-C55-C31	111.02(14)	H60D-C60A-H60E	109.5
O10-C56-C57	111.40(15)	C59A-C60A-H60F	109.5
O10-C56-H56A	109.3	H60D-C60A-H60F	109.5
C57-C56-H56A	109.3	H60E-C60A-H60F	109.5
O10-C56-H56B	109.3	C5-O1-H1O	108.7(17)
C57-C56-H56B	109.3	C9-O2-H2O	109.9(14)
H56A-C56-H56B	108.0	C25-O4-C26	114.69(13)
C56-C57-H57A	109.5	C28-O6-C29	116.65(13)
C56-C57-H57B	109.5	C35-O7-H7O	107.6(15)
H57A-C57-H57B	109.5	C39-O8-H8O	107.1(18)
C56-C57-H57C	109.5	C55-O10-C56	116.27(14)
H57A-C57-H57C	109.5	C58-O12-C59	116.57(14)
H57B-C57-H57C	109.5	C58-O12-C59A	117.4(5)
O11-C58-O12	124.11(16)		

Table 4.6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4.3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	14(1)	16(1)	16(1)	-4(1)	-1(1)	-3(1)
C2	16(1)	19(1)	16(1)	-5(1)	-3(1)	-1(1)
C3	16(1)	15(1)	15(1)	-3(1)	-1(1)	-6(1)
C4	15(1)	14(1)	16(1)	-1(1)	0(1)	-5(1)
C5	14(1)	12(1)	16(1)	-1(1)	0(1)	-1(1)
C6	16(1)	18(1)	19(1)	-4(1)	2(1)	-5(1)
C7	22(1)	20(1)	18(1)	-4(1)	2(1)	-7(1)
C8	16(1)	15(1)	17(1)	-4(1)	0(1)	-2(1)
C9	17(1)	13(1)	17(1)	-2(1)	0(1)	-4(1)
C10	13(1)	15(1)	15(1)	-2(1)	0(1)	-4(1)
C11	12(1)	14(1)	18(1)	-2(1)	0(1)	-4(1)
C12	15(1)	15(1)	16(1)	-4(1)	-2(1)	-2(1)
C13	18(1)	11(1)	18(1)	-1(1)	-3(1)	-1(1)
C14	19(1)	17(1)	20(1)	-1(1)	-1(1)	-2(1)
C15	29(1)	23(1)	17(1)	-3(1)	-2(1)	-1(1)
C16	28(1)	21(1)	25(1)	-5(1)	-13(1)	0(1)
C17	18(1)	20(1)	30(1)	-3(1)	-6(1)	-3(1)
C18	16(1)	19(1)	20(1)	-2(1)	-1(1)	-2(1)
C19	13(1)	18(1)	16(1)	-5(1)	1(1)	-2(1)
C20	21(1)	18(1)	24(1)	-4(1)	-4(1)	-4(1)
C21	24(1)	26(1)	30(1)	-11(1)	-8(1)	-6(1)
C22	24(1)	31(1)	22(1)	-6(1)	-10(1)	-4(1)
C23	23(1)	23(1)	20(1)	0(1)	-3(1)	-3(1)
C24	16(1)	21(1)	17(1)	-6(1)	0(1)	-5(1)
C25	18(1)	15(1)	17(1)	-1(1)	-2(1)	-2(1)
C26	24(1)	25(1)	38(1)	-6(1)	10(1)	-10(1)
C27	29(1)	33(1)	43(1)	-12(1)	13(1)	-11(1)
C28	14(1)	18(1)	17(1)	-3(1)	2(1)	-4(1)
C29	27(1)	12(1)	26(1)	-5(1)	2(1)	0(1)
C30	25(1)	25(1)	31(1)	-9(1)	2(1)	-2(1)
C31	16(1)	18(1)	16(1)	-5(1)	-2(1)	-3(1)

C32	16(1)	18(1)	17(1)	-3(1)	-2(1)	-4(1)
C33	13(1)	16(1)	16(1)	-1(1)	-1(1)	-4(1)
C34	14(1)	15(1)	17(1)	-1(1)	0(1)	-5(1)
C35	16(1)	13(1)	15(1)	0(1)	-2(1)	-5(1)
C36	17(1)	15(1)	17(1)	-3(1)	-2(1)	-3(1)
C37	21(1)	19(1)	17(1)	-2(1)	1(1)	-6(1)
C38	17(1)	18(1)	18(1)	-4(1)	1(1)	-6(1)
C39	15(1)	12(1)	16(1)	0(1)	-3(1)	-2(1)
C40	16(1)	16(1)	14(1)	-2(1)	-2(1)	-5(1)
C41	16(1)	17(1)	15(1)	-3(1)	-1(1)	-5(1)
C42	15(1)	22(1)	18(1)	-5(1)	-3(1)	-2(1)
C43	12(1)	18(1)	14(1)	-5(1)	0(1)	-2(1)
C44	15(1)	19(1)	18(1)	-4(1)	0(1)	-3(1)
C45	18(1)	20(1)	18(1)	-1(1)	-1(1)	1(1)
C46	17(1)	30(1)	18(1)	-8(1)	-4(1)	1(1)
C47	18(1)	26(1)	25(1)	-12(1)	-2(1)	-5(1)
C48	17(1)	17(1)	22(1)	-4(1)	-1(1)	-4(1)
C49	19(1)	13(1)	17(1)	-3(1)	-4(1)	-3(1)
C50	19(1)	18(1)	22(1)	-2(1)	-3(1)	-4(1)
C51	19(1)	20(1)	30(1)	-7(1)	-7(1)	-1(1)
C52	28(1)	22(1)	25(1)	-7(1)	-14(1)	1(1)
C53	30(1)	25(1)	17(1)	-4(1)	-4(1)	-3(1)
C54	20(1)	22(1)	19(1)	-3(1)	-2(1)	-4(1)
C55	15(1)	16(1)	18(1)	-2(1)	-4(1)	1(1)
C56	22(1)	33(1)	25(1)	-2(1)	3(1)	-10(1)
C57	21(1)	42(1)	37(1)	-2(1)	3(1)	-5(1)
C58	18(1)	20(1)	17(1)	-5(1)	1(1)	-5(1)
C59	25(1)	13(1)	27(1)	-4(1)	0(1)	-2(1)
C60	25(1)	21(1)	40(2)	-6(1)	-4(1)	3(1)
O1	17(1)	13(1)	23(1)	-1(1)	-3(1)	-1(1)
O2	21(1)	17(1)	22(1)	-2(1)	3(1)	-8(1)
O3	29(1)	19(1)	37(1)	-9(1)	6(1)	-9(1)
O4	24(1)	25(1)	34(1)	-12(1)	12(1)	-10(1)
O5	24(1)	24(1)	27(1)	-11(1)	-4(1)	-5(1)
O6	22(1)	14(1)	21(1)	-5(1)	-2(1)	1(1)
O7	19(1)	15(1)	23(1)	0(1)	0(1)	-6(1)

O8	18(1)	15(1)	21(1)	1(1)	-4(1)	0(1)
O9	26(1)	21(1)	29(1)	-7(1)	-2(1)	-8(1)
O10	22(1)	30(1)	22(1)	-10(1)	4(1)	-10(1)
O11	24(1)	24(1)	27(1)	-10(1)	-2(1)	-8(1)
O12	28(1)	17(1)	42(1)	-10(1)	-15(1)	3(1)

Table 4.7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4.3a**.

	x	y	z	U(eq)
H2A	3322	5736	8157	21
H2B	2718	4923	8724	21
H6A	5431	4385	6224	21
H6B	6442	3328	6292	21
H7A	5035	4144	4920	24
H7B	6125	3143	4952	24
H8A	5009	2056	5467	20
H8B	4063	2929	4921	20
H12A	1142	5747	6527	19
H12B	2156	6316	6456	19
H14	3868	3416	9293	23
H15	4979	3249	10463	29
H16	6933	3244	10237	30
H17	7769	3347	8828	27
H18	6665	3493	7659	23
H20	1838	3032	5377	25
H21	719	3521	4181	31
H22	469	5157	3408	31
H23	1369	6310	3825	27
H24	2473	5829	5031	21
H26A	-577	4667	9443	34
H26B	-1260	5104	8581	34
H27A	-1479	6207	10021	52
H27B	-2450	5732	9764	52
H27C	-2131	6672	9155	52
H29A	-368	9015	7033	27
H29B	424	8860	7829	27
H30A	-1663	8248	7954	41
H30B	-1573	9279	8273	41
H30C	-897	8185	8745	41
H32A	2972	-1527	8450	20

H32B	3982	-960	8423	20
H36A	1080	2084	9801	20
H36B	141	2884	9196	20
H37A	-984	1848	9831	22
H37B	106	850	9947	22
H38A	-251	417	8694	21
H38B	-1283	1453	8547	21
H42A	2575	-174	6159	22
H42B	1954	-995	6689	22
H44	2551	-917	9924	21
H45	3554	-1271	11178	24
H46	4402	-59	11552	27
H47	4252	1494	10660	27
H48	3258	1855	9407	22
H50	-1461	1149	7151	24
H51	-2595	1475	5969	27
H52	-1776	1781	4572	30
H53	186	1734	4370	29
H54	1334	1361	5548	24
H56A	5826	170	5705	32
H56B	6179	-729	5103	32
H57A	6922	-934	6799	52
H57B	7723	-828	5937	52
H57C	7273	-1833	6199	52
H59A	5757	-3681	6579	27
H59B	5123	-4189	7403	27
H60A	7131	-3503	7479	45
H60B	7151	-4684	7521	45
H60C	6513	-4045	8286	45
H59C	5364	-4133	8156	35
H59D	4892	-4144	7228	35
H60D	6481	-3552	6541	66
H60E	6958	-4634	7111	66
H60F	6959	-3595	7462	66
H2O	2964(18)	2374(15)	7020(14)	24(5)
H7O	1533(18)	3010(16)	8100(13)	23(6)

H8O	60(20)	2930(20)	7358(16)	52(8)
H1O	5050(20)	1700(20)	7148(16)	53(8)

Table 4.8. Torsion angles [°] for **4.3a**.

C25-C1-C2-C3	89.65(15)	C5-C9-C10-C11	-28.50(19)
C28-C1-C2-C3	-149.18(13)	O2-C9-C10-C19	-79.03(17)
C12-C1-C2-C3	-26.12(16)	C8-C9-C10-C19	41.55(19)
C1-C2-C3-C4	-173.99(16)	C5-C9-C10-C19	154.35(14)
C1-C2-C3-C11	12.49(17)	C19-C10-C11-C3	178.68(14)
C11-C3-C4-C13	173.00(14)	C9-C10-C11-C3	1.6(2)
C2-C3-C4-C13	0.2(3)	C19-C10-C11-C12	0.9(3)
C11-C3-C4-C5	0.8(2)	C9-C10-C11-C12	-176.18(15)
C2-C3-C4-C5	-171.97(15)	C4-C3-C11-C10	14.5(2)
C3-C4-C5-O1	-151.98(14)	C2-C3-C11-C10	-171.41(15)
C13-C4-C5-O1	35.61(19)	C4-C3-C11-C12	-167.40(15)
C3-C4-C5-C6	87.98(17)	C2-C3-C11-C12	6.72(17)
C13-C4-C5-C6	-84.43(17)	C10-C11-C12-C1	154.92(16)
C3-C4-C5-C9	-29.1(2)	C3-C11-C12-C1	-23.11(16)
C13-C4-C5-C9	158.45(14)	C25-C1-C12-C11	-85.57(15)
O1-C5-C6-C7	92.79(15)	C28-C1-C12-C11	152.43(13)
C4-C5-C6-C7	-145.57(13)	C2-C1-C12-C11	30.04(16)
C9-C5-C6-C7	-21.28(16)	C3-C4-C13-C14	51.2(2)
C5-C6-C7-C8	-5.09(17)	C5-C4-C13-C14	-136.83(16)
C6-C7-C8-C9	30.39(16)	C3-C4-C13-C18	-126.20(18)
C7-C8-C9-O2	-162.16(13)	C5-C4-C13-C18	45.8(2)
C7-C8-C9-C10	74.76(16)	C18-C13-C14-C15	2.6(2)
C7-C8-C9-C5	-43.52(15)	C4-C13-C14-C15	-174.88(15)
O1-C5-C9-O2	39.99(17)	C13-C14-C15-C16	-0.4(3)
C4-C5-C9-O2	-84.06(16)	C14-C15-C16-C17	-1.4(3)
C6-C5-C9-O2	153.74(13)	C15-C16-C17-C18	1.0(3)
O1-C5-C9-C10	165.83(12)	C16-C17-C18-C13	1.2(3)
C4-C5-C9-C10	41.78(18)	C14-C13-C18-C17	-3.0(2)
C6-C5-C9-C10	-80.43(15)	C4-C13-C18-C17	174.49(15)
O1-C5-C9-C8	-74.39(14)	C11-C10-C19-C20	-129.66(17)
C4-C5-C9-C8	161.55(13)	C9-C10-C19-C20	47.4(2)
C6-C5-C9-C8	39.35(14)	C11-C10-C19-C24	49.7(2)
O2-C9-C10-C11	98.12(17)	C9-C10-C19-C24	-133.23(16)
C8-C9-C10-C11	-141.29(15)	C24-C19-C20-C21	-1.1(2)

C10-C19-C20-C21	178.26(16)	C39-C35-C36-C37	44.88(15)
C19-C20-C21-C22	0.5(3)	C35-C36-C37-C38	-30.20(16)
C20-C21-C22-C23	0.5(3)	C36-C37-C38-C39	3.67(17)
C21-C22-C23-C24	-0.8(3)	C37-C38-C39-O8	-90.01(14)
C22-C23-C24-C19	0.2(3)	C37-C38-C39-C40	147.42(13)
C20-C19-C24-C23	0.8(2)	C37-C38-C39-C35	23.53(16)
C10-C19-C24-C23	-178.62(15)	O7-C35-C39-O8	-50.58(17)
C28-C1-C25-O3	165.81(16)	C34-C35-C39-O8	-169.35(12)
C12-C1-C25-O3	41.5(2)	C36-C35-C39-O8	70.56(15)
C2-C1-C25-O3	-71.3(2)	O7-C35-C39-C40	72.80(17)
C28-C1-C25-O4	-14.90(19)	C34-C35-C39-C40	-45.96(17)
C12-C1-C25-O4	-139.20(14)	C36-C35-C39-C40	-166.05(13)
C2-C1-C25-O4	107.99(15)	O7-C35-C39-C38	-162.90(13)
C25-C1-C28-O5	101.29(18)	C34-C35-C39-C38	78.33(15)
C12-C1-C28-O5	-137.11(16)	C36-C35-C39-C38	-41.76(14)
C2-C1-C28-O5	-19.3(2)	O8-C39-C40-C41	151.26(14)
C25-C1-C28-O6	-77.85(16)	C38-C39-C40-C41	-88.41(18)
C12-C1-C28-O6	43.75(18)	C35-C39-C40-C41	29.2(2)
C2-C1-C28-O6	161.54(13)	O8-C39-C40-C49	-31.48(19)
C58-C31-C32-C33	-152.50(13)	C38-C39-C40-C49	88.85(17)
C55-C31-C32-C33	87.45(15)	C35-C39-C40-C49	-153.54(14)
C42-C31-C32-C33	-30.72(16)	C49-C40-C41-C33	-174.36(15)
C31-C32-C33-C34	-151.72(16)	C39-C40-C41-C33	2.7(2)
C31-C32-C33-C41	25.09(16)	C49-C40-C41-C42	-1.4(3)
C41-C33-C34-C43	-178.45(15)	C39-C40-C41-C42	175.64(15)
C32-C33-C34-C43	-2.1(3)	C34-C33-C41-C40	-18.2(2)
C41-C33-C34-C35	-2.1(2)	C32-C33-C41-C40	164.80(15)
C32-C33-C34-C35	174.30(15)	C34-C33-C41-C42	167.57(15)
C33-C34-C35-O7	-89.71(16)	C32-C33-C41-C42	-9.43(17)
C43-C34-C35-O7	86.78(16)	C40-C41-C42-C31	176.18(16)
C33-C34-C35-C36	145.60(15)	C33-C41-C42-C31	-10.21(17)
C43-C34-C35-C36	-37.92(19)	C58-C31-C42-C41	146.10(14)
C33-C34-C35-C39	32.82(19)	C55-C31-C42-C41	-92.98(15)
C43-C34-C35-C39	-150.70(14)	C32-C31-C42-C41	25.23(16)
O7-C35-C36-C37	165.67(13)	C33-C34-C43-C48	128.89(17)
C34-C35-C36-C37	-73.43(16)	C35-C34-C43-C48	-47.4(2)

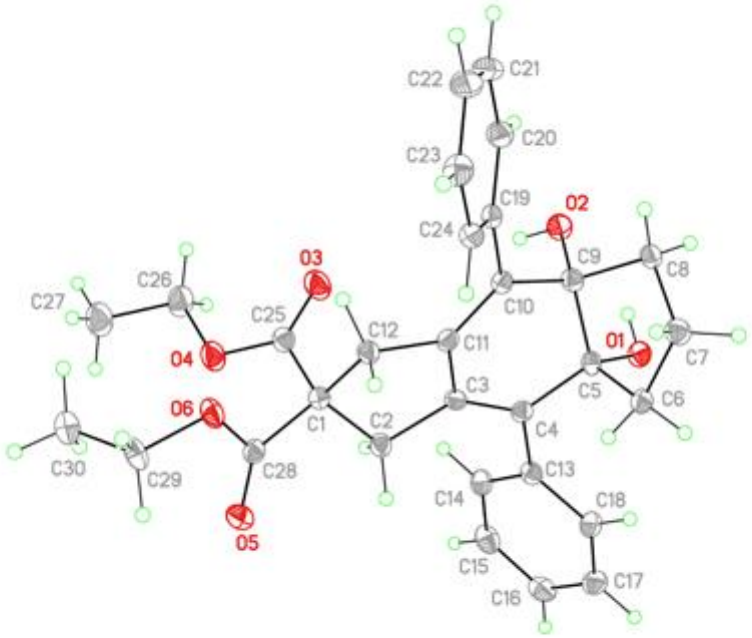
C33-C34-C43-C44	-51.3(2)	C58-C31-C55-O10	38.53(18)
C35-C34-C43-C44	132.42(16)	C32-C31-C55-O10	160.28(13)
C48-C43-C44-C45	-0.5(2)	C42-C31-C55-O10	-84.90(16)
C34-C43-C44-C45	179.66(15)	C55-C31-C58-O11	-123.12(18)
C43-C44-C45-C46	0.4(2)	C32-C31-C58-O11	115.80(18)
C44-C45-C46-C47	-0.2(2)	C42-C31-C58-O11	-1.3(2)
C45-C46-C47-C48	0.1(3)	C55-C31-C58-O12	57.49(17)
C46-C47-C48-C43	-0.3(3)	C32-C31-C58-O12	-63.59(17)
C44-C43-C48-C47	0.4(2)	C42-C31-C58-O12	179.36(14)
C34-C43-C48-C47	-179.73(15)	O3-C25-O4-C26	-2.8(2)
C41-C40-C49-C54	-53.5(2)	C1-C25-O4-C26	177.86(14)
C39-C40-C49-C54	129.45(16)	C27-C26-O4-C25	-169.34(16)
C41-C40-C49-C50	127.80(18)	O5-C28-O6-C29	-7.8(2)
C39-C40-C49-C50	-49.2(2)	C1-C28-O6-C29	171.32(13)
C54-C49-C50-C51	0.6(2)	C30-C29-O6-C28	-87.99(18)
C40-C49-C50-C51	179.33(15)	O9-C55-O10-C56	5.6(2)
C49-C50-C51-C52	-1.0(3)	C31-C55-O10-C56	-175.54(13)
C50-C51-C52-C53	0.5(3)	C57-C56-O10-C55	75.3(2)
C51-C52-C53-C54	0.5(3)	O11-C58-O12-C59	12.7(3)
C52-C53-C54-C49	-0.9(3)	C31-C58-O12-C59	-167.91(17)
C50-C49-C54-C53	0.4(2)	O11-C58-O12-C59A	-13.4(6)
C40-C49-C54-C53	-178.35(16)	C31-C58-O12-C59A	166.0(5)
C58-C31-C55-O9	-142.63(16)	C60-C59-O12-C58	176.58(18)
C32-C31-C55-O9	-20.9(2)	C60A-C59A-O12-C58	127.5(7)
C42-C31-C55-O9	93.95(19)		

Table 4.9. Hydrogen bonds for **4.3a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O2-H2O...O7	0.83(2)	1.98(2)	2.7993(18)	168.7(19)
O7-H7O...O3	0.79(2)	1.97(2)	2.7467(18)	169(2)
O1-H1O...O2	0.85(3)	2.22(3)	2.7356(17)	119(2)
O1-H1O...O9	0.85(3)	2.35(3)	3.1149(17)	150(2)

Symmetry transformations used to generate equivalent atoms:

Figure 4.2. View of **4.3a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **Ru-Complex II**-$CHCl_3$:

Crystals grew as colorless prisms by slow evaporation from $CHCl_3$. The data crystal was cut from a larger crystal and had approximate dimensions; 0.25 x 0.18 x 0.14 mm. The data were collected on a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD using a graphite monochromator with MoKα radiation (γ = 0.71073Å). A total of 1080 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 24 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 4.10. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[17] The structure was solved by direct methods using SIR20042 and refined by full-matrix least-squares on F[18] with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[19] Structure analysis was aided by use of the programs PLATON98[20] and WinGX.[21] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to oxygen were located in a ΔF map and refined with isotropic displacement parameters.

The ethyl group on one ethyl ester portion of molecule 2 was disordered. The disorder was modeled by assigning the variable x to the site occupancy factors to C59 and C60, while (1-x) was assigned to the site occupancy factors for C59a and C60a. The geometry of the two pairs of atoms was restrained to be equivalent throughout the refinement process. A common isotropic displacement parameter was refined for the four atoms while refining the variable x. The major component of the disorder refined to a site occupancy of 81(2)%.

The function, $\sum w(|Fo|^2 - |Fc|^2)$,15 was minimized, where $w = 1/[(\sum(Fo))^2 + (0.0475*P)^2 + (1.3113*P)]$ and $P = (|Fo|^2 + {}^2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.127, with R(F) equal to 0.0521 and a

goodness of fit, S, = 1.04. Definitions used for calculating R(F), Rw(F^2) and the goodness of fit, S, are given below.[22] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[23] All figures were generated using SHELXTL/PC.[24] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 4.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **Ru-Complex II**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	4809(1)	1402(2)	3168(1)	14(1)
C2	4262(1)	1981(2)	3004(1)	14(1)
C3	3940(1)	1932(2)	3367(1)	14(1)
C4	3326(1)	1985(2)	3421(1)	17(1)
C5	3352(1)	1710(2)	3938(1)	16(1)
C6	3950(1)	1209(2)	4117(1)	16(1)
C7	4292(1)	1519(2)	3761(1)	12(1)
C8	4850(1)	1292(2)	3672(1)	14(1)
C9	4046(1)	2170(2)	2512(1)	15(1)
C10	3485(1)	1885(2)	2310(1)	18(1)
C11	3283(1)	2052(2)	1844(1)	21(1)
C12	3630(1)	2511(2)	1573(1)	22(1)
C13	4190(1)	2790(2)	1769(1)	20(1)
C14	4396(1)	2608(2)	2231(1)	17(1)
C15	2876(1)	927(2)	3999(1)	17(1)
C16	2502(1)	-819(2)	3851(1)	26(1)
C17	2660(1)	-1825(2)	3631(1)	26(1)
C18	3239(1)	2691(2)	4214(1)	18(1)
C19	3361(1)	3376(3)	4982(1)	27(1)
C20	3899(1)	3532(3)	5326(1)	34(1)
C21	5312(1)	769(2)	3996(1)	14(1)
C22	5316(1)	804(2)	4468(1)	18(1)
C23	5748(1)	307(2)	4780(1)	22(1)
C24	6188(1)	-221(2)	4627(1)	25(1)
C25	6189(1)	-254(2)	4159(1)	23(1)
C26	5759(1)	232(2)	3845(1)	18(1)
C27	4212(1)	5676(2)	3876(1)	16(1)
C28	3960(1)	5355(2)	4240(1)	18(1)
C29	3900(1)	6060(2)	4590(1)	24(1)
C30	4102(1)	7095(2)	4580(1)	25(1)

C31	4360(1)	7422(2)	4224(1)	25(1)
C32	4416(1)	6722(2)	3870(1)	20(1)
C33	3531(1)	4870(2)	3053(1)	15(1)
C34	3449(1)	4513(2)	2600(1)	17(1)
C35	2925(1)	4642(2)	2308(1)	20(1)
C36	2476(1)	5141(2)	2463(1)	20(1)
C37	2551(1)	5493(2)	2915(1)	20(1)
C38	3074(1)	5355(2)	3209(1)	19(1)
C39	4699(1)	5416(2)	3070(1)	15(1)
C40	5318(1)	5287(2)	3319(1)	14(1)
C41	6132(1)	3823(2)	3837(1)	15(1)
C42	6232(1)	3037(2)	4171(1)	17(1)
C43	6765(1)	2959(2)	4461(1)	22(1)
C44	7193(1)	3679(2)	4417(1)	22(1)
C45	7093(1)	4484(2)	4091(1)	21(1)
C46	6567(1)	4547(2)	3799(1)	18(1)
C47	5762(1)	3484(2)	2908(1)	14(1)
C48	6108(1)	2586(2)	2931(1)	17(1)
C49	6365(1)	2315(2)	2565(1)	20(1)
C50	6264(1)	2922(2)	2167(1)	22(1)
C51	5910(1)	3813(2)	2139(1)	21(1)
C52	5661(1)	4097(2)	2508(1)	18(1)
C53	4853(1)	3480(2)	4214(1)	17(1)
O1	5158(1)	1109(1)	2932(1)	17(1)
O2	2505(1)	1129(2)	4208(1)	31(1)
O3	2927(1)	-8(1)	3795(1)	21(1)
O4	2952(1)	3439(2)	4054(1)	26(1)
O5	3478(1)	2585(2)	4654(1)	23(1)
O6	4973(1)	3688(2)	4597(1)	26(1)
P1	4241(1)	4728(1)	3410(1)	13(1)
P2	5467(1)	3857(1)	3414(1)	12(1)
Ru1	4652(1)	3058(1)	3602(1)	10(1)

Table 4.11. Bond lengths [Å] and angles [°] for **Ru-Complex II**.

C1-O1	1.241(3)	C15-O2	1.201(3)
C1-C8	1.492(3)	C15-O3	1.338(3)
C1-C2	1.495(3)	C16-O3	1.470(3)
C1-Ru1	2.511(2)	C16-C17	1.503(4)
C2-C3	1.440(4)	C16-H16A	0.99
C2-C9	1.477(3)	C16-H16B	0.99
C2-Ru1	2.291(2)	C17-H17A	0.98
C3-C7	1.410(3)	C17-H17B	0.98
C3-C4	1.505(4)	C17-H17C	0.98
C3-Ru1	2.222(2)	C18-O4	1.208(3)
C4-C5	1.568(3)	C18-O5	1.335(3)
C4-H4A	0.99	C19-O5	1.454(3)
C4-H4B	0.99	C19-C20	1.499(4)
C5-C18	1.531(4)	C19-H19A	0.99
C5-C15	1.538(3)	C19-H19B	0.99
C5-C6	1.560(3)	C20-H20A	0.98
C6-C7	1.503(3)	C20-H20B	0.98
C6-H6A	0.99	C20-H20C	0.98
C6-H6B	0.99	C21-C22	1.404(4)
C7-C8	1.434(3)	C21-C26	1.405(4)
C7-Ru1	2.200(2)	C22-C23	1.399(3)
C8-C21	1.476(3)	C22-H22	0.95
C8-Ru1	2.266(2)	C23-C24	1.388(4)
C9-C14	1.400(4)	C23-H23	0.95
C9-C10	1.408(4)	C24-C25	1.395(4)
C10-C11	1.396(4)	C24-H24	0.95
C10-H10	0.95	C25-C26	1.394(4)
C11-C12	1.386(4)	C25-H25	0.95
C11-H11	0.95	C26-H26	0.95
C12-C13	1.401(4)	C27-C28	1.393(4)
C12-H12	0.95	C27-C32	1.402(4)
C13-C14	1.391(4)	C27-P1	1.841(2)
C13-H13	0.95	C28-C29	1.391(4)
C14-H14	0.95	C28-H28	0.95

C29-C30	1.388(4)	C41-C46	1.401(3)
C29-H29	0.95	C41-P2	1.833(3)
C30-C31	1.383(4)	C42-C43	1.402(4)
C30-H30	0.95	C42-H42	0.95
C31-C32	1.396(4)	C43-C44	1.388(4)
C31-H31	0.95	C43-H43	0.95
C32-H32	0.95	C44-C45	1.391(4)
C33-C34	1.400(3)	C44-H44	0.95
C33-C38	1.402(4)	C45-C46	1.389(4)
C33-P1	1.834(3)	C45-H45	0.95
C34-C35	1.393(3)	C46-H46	0.95
C34-H34	0.95	C47-C48	1.391(3)
C35-C36	1.391(4)	C47-C52	1.400(3)
C35-H35	0.95	C47-P2	1.839(2)
C36-C37	1.394(4)	C48-C49	1.389(4)
C36-H36	0.95	C48-H48	0.95
C37-C38	1.395(3)	C49-C50	1.390(4)
C37-H37	0.95	C49-H49	0.95
C38-H38	0.95	C50-C51	1.394(4)
C39-C40	1.535(3)	C50-H50	0.95
C39-P1	1.835(2)	C51-C52	1.391(4)
C39-H39A	0.99	C51-H51	0.95
C39-H39B	0.99	C52-H52	0.95
C40-P2	1.840(2)	C53-O6	1.154(3)
C40-H40A	0.99	C53-Ru1	1.871(3)
C40-H40B	0.99	P1-Ru1	2.3398(6)
C41-C42	1.390(3)	P2-Ru1	2.3458(6)

O1-C1-C8	128.1(2)	C9-C2-C1	121.7(2)
O1-C1-C2	126.5(2)	C3-C2-Ru1	68.83(13)
C8-C1-C2	105.3(2)	C9-C2-Ru1	133.87(16)
O1-C1-Ru1	135.75(16)	C1-C2-Ru1	80.10(13)
C8-C1-Ru1	63.07(12)	C7-C3-C2	108.7(2)
C2-C1-Ru1	64.00(12)	C7-C3-C4	111.7(2)
C3-C2-C9	127.7(2)	C2-C3-C4	138.2(2)
C3-C2-C1	106.8(2)	C7-C3-Ru1	70.55(13)

C2-C3-Ru1	74.01(14)	C11-C10-H10	119.6
C4-C3-Ru1	129.92(16)	C9-C10-H10	119.6
C3-C4-C5	103.5(2)	C12-C11-C10	120.4(3)
C3-C4-H4A	111.1	C12-C11-H11	119.8
C5-C4-H4A	111.1	C10-C11-H11	119.8
C3-C4-H4B	111.1	C11-C12-C13	119.3(2)
C5-C4-H4B	111.1	C11-C12-H12	120.4
H4A-C4-H4B	109.0	C13-C12-H12	120.4
C18-C5-C15	104.0(2)	C14-C13-C12	120.3(2)
C18-C5-C6	112.5(2)	C14-C13-H13	119.8
C15-C5-C6	110.6(2)	C12-C13-H13	119.8
C18-C5-C4	111.7(2)	C13-C14-C9	121.0(2)
C15-C5-C4	111.2(2)	C13-C14-H14	119.5
C6-C5-C4	106.97(19)	C9-C14-H14	119.5
C7-C6-C5	103.71(19)	O2-C15-O3	124.0(2)
C7-C6-H6A	111.0	O2-C15-C5	124.1(2)
C5-C6-H6A	111.0	O3-C15-C5	112.0(2)
C7-C6-H6B	111.0	O3-C16-C17	107.3(2)
C5-C6-H6B	111.0	O3-C16-H16A	110.3
H6A-C6-H6B	109.0	C17-C16-H16A	110.3
C3-C7-C8	110.5(2)	O3-C16-H16B	110.3
C3-C7-C6	111.3(2)	C17-C16-H16B	110.3
C8-C7-C6	136.3(2)	H16A-C16-H16B	108.5
C3-C7-Ru1	72.26(13)	C16-C17-H17A	109.5
C8-C7-Ru1	73.81(13)	C16-C17-H17B	109.5
C6-C7-Ru1	131.58(16)	H17A-C17-H17B	109.5
C7-C8-C21	125.1(2)	C16-C17-H17C	109.5
C7-C8-C1	106.1(2)	H17A-C17-H17C	109.5
C21-C8-C1	126.8(2)	H17B-C17-H17C	109.5
C7-C8-Ru1	68.78(12)	O4-C18-O5	124.9(2)
C21-C8-Ru1	127.73(16)	O4-C18-C5	123.9(2)
C1-C8-Ru1	80.99(13)	O5-C18-C5	111.1(2)
C14-C9-C10	118.0(2)	O5-C19-C20	107.6(2)
C14-C9-C2	121.1(2)	O5-C19-H19A	110.2
C10-C9-C2	120.9(2)	C20-C19-H19A	110.2
C11-C10-C9	120.9(3)	O5-C19-H19B	110.2

C20-C19-H19B	110.2	C31-C30-H30	120.0
H19A-C19-H19B	108.5	C29-C30-H30	120.0
C19-C20-H20A	109.5	C30-C31-C32	120.7(3)
C19-C20-H20B	109.5	C30-C31-H31	119.6
H20A-C20-H20B	109.5	C32-C31-H31	119.6
C19-C20-H20C	109.5	C31-C32-C27	119.8(3)
H20A-C20-H20C	109.5	C31-C32-H32	120.1
H20B-C20-H20C	109.5	C27-C32-H32	120.1
C22-C21-C26	118.0(2)	C34-C33-C38	118.6(2)
C22-C21-C8	120.3(2)	C34-C33-P1	118.42(18)
C26-C21-C8	121.6(2)	C38-C33-P1	122.96(19)
C23-C22-C21	121.2(2)	C35-C34-C33	120.8(2)
C23-C22-H22	119.4	C35-C34-H34	119.6
C21-C22-H22	119.4	C33-C34-H34	119.6
C24-C23-C22	120.3(3)	C36-C35-C34	120.3(2)
C24-C23-H23	119.8	C36-C35-H35	119.9
C22-C23-H23	119.8	C34-C35-H35	119.9
C23-C24-C25	118.9(2)	C35-C36-C37	119.6(2)
C23-C24-H24	120.5	C35-C36-H36	120.2
C25-C24-H24	120.5	C37-C36-H36	120.2
C26-C25-C24	121.2(2)	C36-C37-C38	120.3(2)
C26-C25-H25	119.4	C36-C37-H37	119.9
C24-C25-H25	119.4	C38-C37-H37	119.9
C25-C26-C21	120.3(2)	C37-C38-C33	120.5(2)
C25-C26-H26	119.8	C37-C38-H38	119.7
C21-C26-H26	119.8	C33-C38-H38	119.7
C28-C27-C32	118.8(2)	C40-C39-P1	107.70(16)
C28-C27-P1	118.90(19)	C40-C39-H39A	110.2
C32-C27-P1	122.2(2)	P1-C39-H39A	110.2
C29-C28-C27	121.1(2)	C40-C39-H39B	110.2
C29-C28-H28	119.5	P1-C39-H39B	110.2
C27-C28-H28	119.5	H39A-C39-H39B	108.5
C30-C29-C28	119.7(3)	C39-C40-P2	108.50(16)
C30-C29-H29	120.1	C39-C40-H40A	110.0
C28-C29-H29	120.1	P2-C40-H40A	110.0
C31-C30-C29	119.9(3)	C39-C40-H40B	110.0

P2-C40-H40B	110.0	C51-C52-H52	120.0
H40A-C40-H40B	108.4	C47-C52-H52	120.0
C42-C41-C46	119.0(2)	O6-C53-Ru1	176.6(2)
C42-C41-P2	121.36(19)	C15-O3-C16	115.6(2)
C46-C41-P2	119.41(19)	C18-O5-C19	119.4(2)
C41-C42-C43	120.5(2)	C33-P1-C39	102.49(11)
C41-C42-H42	119.8	C33-P1-C27	102.31(11)
C43-C42-H42	119.8	C39-P1-C27	102.79(11)
C44-C43-C42	119.8(2)	C33-P1-Ru1	121.98(8)
C44-C43-H43	120.1	C39-P1-Ru1	106.91(8)
C42-C43-H43	120.1	C27-P1-Ru1	117.84(8)
C43-C44-C45	120.2(2)	C41-P2-C47	98.08(11)
C43-C44-H44	119.9	C41-P2-C40	104.23(11)
C45-C44-H44	119.9	C47-P2-C40	102.35(11)
C46-C45-C44	119.8(2)	C41-P2-Ru1	118.51(8)
C46-C45-H45	120.1	C47-P2-Ru1	123.18(7)
C44-C45-H45	120.1	C40-P2-Ru1	108.04(8)
C45-C46-C41	120.7(2)	C53-Ru1-C7	94.54(10)
C45-C46-H46	119.7	C53-Ru1-C3	122.03(10)
C41-C46-H46	119.7	C7-Ru1-C3	37.19(9)
C48-C47-C52	119.6(2)	C53-Ru1-C8	100.13(9)
C48-C47-P2	118.74(18)	C7-Ru1-C8	37.41(8)
C52-C47-P2	121.66(19)	C3-Ru1-C8	62.73(8)
C49-C48-C47	120.3(2)	C53-Ru1-C2	156.55(10)
C49-C48-H48	119.8	C7-Ru1-C2	62.06(8)
C47-C48-H48	119.8	C3-Ru1-C2	37.16(9)
C48-C49-C50	120.1(2)	C8-Ru1-C2	62.81(8)
C48-C49-H49	119.9	C53-Ru1-P1	90.29(7)
C50-C49-H49	119.9	C7-Ru1-P1	132.49(6)
C49-C50-C51	119.9(3)	C3-Ru1-P1	103.29(6)
C49-C50-H50	120.0	C8-Ru1-P1	165.60(6)
C51-C50-H50	120.0	C2-Ru1-P1	104.22(6)
C52-C51-C50	120.0(2)	C53-Ru1-P2	92.09(8)
C52-C51-H51	120.0	C7-Ru1-P2	143.22(6)
C50-C51-H51	120.0	C3-Ru1-P2	144.73(7)
C51-C52-C47	120.0(2)	C8-Ru1-P2	105.82(6)

C2-Ru1-P2	107.58(7)	C8-Ru1-C1	35.94(8)
P1-Ru1-P2	83.51(2)	C2-Ru1-C1	35.91(8)
C53-Ru1-C1	134.37(9)	P1-Ru1-C1	135.28(6)
C7-Ru1-C1	59.09(8)	P2-Ru1-C1	91.27(6)
C3-Ru1-C1	59.35(8)		

Table 4.12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Ru-Complex II**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	18(1)	7(1)	15(1)	-1(1)	0(1)	-3(1)
C2	16(1)	11(1)	13(1)	-1(1)	-1(1)	-3(1)
C3	15(1)	9(1)	16(1)	-2(1)	-1(1)	-3(1)
C4	16(1)	16(1)	18(1)	2(1)	1(1)	0(1)
C5	14(1)	14(1)	18(1)	1(1)	0(1)	-1(1)
C6	16(1)	17(1)	15(1)	3(1)	0(1)	0(1)
C7	12(1)	6(1)	17(1)	1(1)	-2(1)	-2(1)
C8	17(1)	6(1)	16(1)	-2(1)	-1(1)	-1(1)
C9	21(1)	6(1)	14(1)	0(1)	-1(1)	2(1)
C10	21(1)	12(1)	18(1)	-1(1)	-1(1)	0(1)
C11	21(1)	18(1)	19(1)	-3(1)	-6(1)	3(1)
C12	34(1)	17(1)	13(1)	-1(1)	-3(1)	8(1)
C13	32(1)	13(1)	14(1)	2(1)	5(1)	4(1)
C14	22(1)	12(1)	17(1)	-2(1)	1(1)	2(1)
C15	18(1)	17(1)	15(1)	-1(1)	0(1)	-4(1)
C16	30(1)	20(1)	30(1)	-5(1)	11(1)	-11(1)
C17	34(2)	16(1)	29(2)	-1(1)	10(1)	-6(1)
C18	17(1)	17(1)	17(1)	1(1)	0(1)	-3(1)
C19	28(1)	28(2)	24(1)	-8(1)	3(1)	4(1)
C20	40(2)	40(2)	21(1)	-12(1)	1(1)	0(1)
C21	16(1)	7(1)	18(1)	1(1)	-2(1)	-1(1)
C22	19(1)	14(1)	20(1)	2(1)	-1(1)	1(1)
C23	28(1)	17(1)	18(1)	2(1)	-5(1)	0(1)
C24	23(1)	18(1)	30(1)	6(1)	-5(1)	3(1)
C25	19(1)	16(1)	33(2)	2(1)	0(1)	4(1)
C26	19(1)	12(1)	20(1)	0(1)	-1(1)	-1(1)
C27	17(1)	14(1)	16(1)	-2(1)	-5(1)	4(1)
C28	20(1)	15(1)	18(1)	-3(1)	-1(1)	3(1)
C29	27(1)	25(1)	19(1)	-4(1)	3(1)	3(1)
C30	30(1)	20(1)	20(1)	-8(1)	-4(1)	7(1)
C31	33(1)	12(1)	28(1)	-6(1)	-1(1)	0(1)

C32	24(1)	13(1)	22(1)	-3(1)	1(1)	2(1)
C33	20(1)	8(1)	17(1)	2(1)	0(1)	0(1)
C34	21(1)	11(1)	18(1)	-1(1)	-2(1)	3(1)
C35	26(1)	14(1)	17(1)	-3(1)	-6(1)	-1(1)
C36	18(1)	14(1)	23(1)	3(1)	-6(1)	-2(1)
C37	17(1)	19(1)	24(1)	0(1)	1(1)	2(1)
C38	22(1)	17(1)	16(1)	2(1)	0(1)	2(1)
C39	19(1)	11(1)	17(1)	2(1)	2(1)	2(1)
C40	17(1)	9(1)	15(1)	0(1)	0(1)	0(1)
C41	18(1)	12(1)	14(1)	-3(1)	0(1)	1(1)
C42	17(1)	16(1)	15(1)	0(1)	-1(1)	-1(1)
C43	23(1)	25(1)	16(1)	4(1)	0(1)	2(1)
C44	16(1)	33(1)	14(1)	-3(1)	-5(1)	-2(1)
C45	19(1)	23(1)	20(1)	-6(1)	0(1)	-6(1)
C46	20(1)	16(1)	18(1)	0(1)	1(1)	-4(1)
C47	16(1)	13(1)	12(1)	-2(1)	-1(1)	-4(1)
C48	20(1)	10(1)	18(1)	-2(1)	-4(1)	-2(1)
C49	19(1)	13(1)	27(1)	-5(1)	4(1)	-1(1)
C50	23(1)	21(1)	23(1)	-8(1)	5(1)	-6(1)
C51	26(1)	22(1)	17(1)	2(1)	4(1)	-3(1)
C52	21(1)	14(1)	19(1)	0(1)	2(1)	-1(1)
C53	16(1)	11(1)	22(1)	0(1)	0(1)	2(1)
O1	20(1)	14(1)	16(1)	-4(1)	3(1)	-1(1)
O2	28(1)	28(1)	43(1)	-13(1)	19(1)	-10(1)
O3	23(1)	15(1)	28(1)	-2(1)	8(1)	-6(1)
O4	28(1)	22(1)	25(1)	-1(1)	-2(1)	7(1)
O5	29(1)	20(1)	17(1)	-2(1)	-2(1)	5(1)
O6	29(1)	32(1)	11(1)	-5(1)	-5(1)	7(1)
P1	15(1)	9(1)	13(1)	0(1)	-1(1)	1(1)
P2	14(1)	8(1)	12(1)	0(1)	-1(1)	-1(1)
Ru1	13(1)	7(1)	9(1)	0(1)	-2(1)	0(1)

Table 4.13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **Ru-Complex II**.

	x	y	z	U(eq)
H4A	3091	1459	3221	20
H4B	3166	2706	3348	20
H6A	4122	1503	4420	19
H6B	3924	424	4141	19
H10	3241	1576	2493	21
H11	2904	1849	1713	25
H12	3490	2635	1257	27
H13	4431	3106	1586	24
H14	4779	2783	2358	21
H16A	2116	-582	3703	31
H16B	2502	-942	4180	31
H17A	2677	-1684	3310	39
H17B	2373	-2375	3648	39
H17C	3033	-2073	3791	39
H19A	3051	3125	5135	33
H19B	3242	4056	4824	33
H20A	4027	2845	5464	51
H20B	3826	4024	5564	51
H20C	4194	3830	5174	51
H22	5021	1171	4577	22
H23	5740	332	5097	26
H24	6483	-556	4838	30
H25	6490	-613	4051	28
H26	5768	199	3527	21
H28	3827	4644	4251	22
H29	3722	5833	4833	28
H30	4064	7579	4818	29
H31	4500	8130	4220	30
H32	4593	6954	3627	24
H34	3754	4178	2490	21

H35	2874	4389	2003	24
H36	2122	5241	2262	24
H37	2245	5828	3023	24
H38	3120	5590	3517	22
H39A	4649	5101	2761	19
H39B	4597	6181	3040	19
H40A	5377	5668	3616	17
H40B	5581	5594	3132	17
H42	5938	2550	4204	20
H43	6833	2415	4686	26
H44	7556	3622	4611	26
H45	7382	4989	4067	25
H46	6503	5086	3571	22
H48	6168	2155	3198	20
H49	6610	1714	2586	24
H50	6435	2730	1915	27
H51	5840	4227	1867	26
H52	5421	4706	2489	22

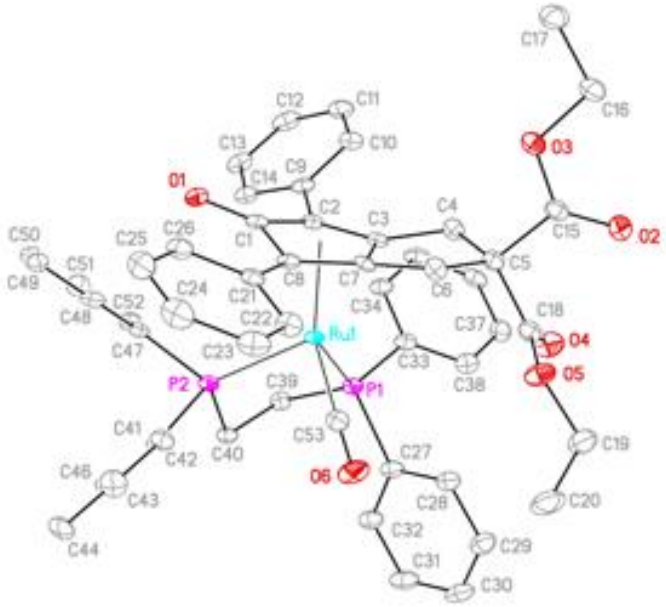
Table 4.14. Torsion angles [°] for **Ru-Complex II**.

O1-C1-C2-C3	166.7(2)		
C8-C1-C2-C3	-15.2(2)	C5-C6-C7-C3	-12.0(2)
Ru1-C1-C2-C3	-64.16(15)	C5-C6-C7-C8	-174.3(3)
O1-C1-C2-C9	6.9(3)	C5-C6-C7-Ru1	72.8(2)
C8-C1-C2-C9	-175.0(2)	C3-C7-C8-C21	-174.6(2)
Ru1-C1-C2-C9	136.0(2)	C6-C7-C8-C21	-12.2(4)
O1-C1-C2-Ru1	-129.1(2)	Ru1-C7-C8-C21	122.0(2)
C8-C1-C2-Ru1	48.99(15)	C3-C7-C8-C1	-9.9(2)
C9-C2-C3-C7	167.8(2)	C6-C7-C8-C1	152.5(3)
C1-C2-C3-C7	9.5(2)	Ru1-C7-C8-C1	-73.32(15)
Ru1-C2-C3-C7	-62.42(15)	C3-C7-C8-Ru1	63.43(15)
C9-C2-C3-C4	3.1(4)	C6-C7-C8-Ru1	-134.1(3)
C1-C2-C3-C4	-155.1(3)	O1-C1-C8-C7	-166.8(2)
Ru1-C2-C3-C4	132.9(3)	C2-C1-C8-C7	15.2(2)
C9-C2-C3-Ru1	-129.8(2)	Ru1-C1-C8-C7	64.71(14)
C1-C2-C3-Ru1	71.95(15)	O1-C1-C8-C21	-2.4(4)
C7-C3-C4-C5	8.5(2)	C2-C1-C8-C21	179.6(2)
C2-C3-C4-C5	172.8(2)	Ru1-C1-C8-C21	-130.9(2)
Ru1-C3-C4-C5	-73.8(2)	O1-C1-C8-Ru1	128.5(2)
C3-C4-C5-C18	108.0(2)	C2-C1-C8-Ru1	-49.52(15)
C3-C4-C5-C15	-136.3(2)	C3-C2-C9-C14	154.5(2)
C3-C4-C5-C6	-15.5(2)	C1-C2-C9-C14	-50.2(3)
C18-C5-C6-C7	-106.3(2)	Ru1-C2-C9-C14	58.1(3)
C15-C5-C6-C7	137.9(2)	C3-C2-C9-C10	-27.3(4)
C4-C5-C6-C7	16.7(2)	C1-C2-C9-C10	128.0(2)
C2-C3-C7-C8	0.2(2)	Ru1-C2-C9-C10	-123.7(2)
C4-C3-C7-C8	169.30(19)	C14-C9-C10-C11	-1.0(4)
Ru1-C3-C7-C8	-64.40(16)	C2-C9-C10-C11	-179.3(2)
C2-C3-C7-C6	-166.82(19)		
C4-C3-C7-C6	2.2(3)		
Ru1-C3-C7-C6	128.54(18)		
C2-C3-C7-Ru1	64.64(15)		
C4-C3-C7-Ru1	-126.30(18)		

C6-C5-C15-O2	123.6(3)
C4-C5-C15-O2	-117.8(3)
C18-C5-C15-O3	-177.1(2)
C6-C5-C15-O3	-56.1(3)
C4-C5-C15-O3	62.6(3)
C15-C5-C18-O4	-92.1(3)
C6-C5-C18-O4	148.2(3)
C4-C5-C18-O4	27.9(3)
C15-C5-C18-O5	85.1(2)
C6-C5-C18-O5	-34.6(3)
C4-C5-C18-O5	-154.9(2)
C7-C8-C21-C22	-23.7(3)
C1-C8-C21-C22	174.7(2)
Ru1-C8-C21-C22	65.4(3)
C7-C8-C21-C26	156.7(2)
C1-C8-C21-C26	-4.9(4)
Ru1-C8-C21-C26	-114.2(2)
C26-C21-C22-C23	-0.8(4)
C8-C21-C22-C23	179.6(2)
C21-C22-C23-C24	0.8(4)
C22-C23-C24-C25	-0.3(4)
C23-C24-C25-C26	-0.1(4)
C24-C25-C26-C21	0.1(4)
C22-C21-C26-C25	0.4(3)
C8-C21-C26-C25	179.9(2)
C32-C27-C28-C29	1.2(4)
P1-C27-C28-C29	-176.6(2)
C27-C28-C29-C30	-1.0(4)
C28-C29-C30-C31	0.2(4)
C29-C30-C31-C32	0.4(4)
C30-C31-C32-C27	-0.2(4)
C28-C27-C32-C31	-0.6(4)
P1-C27-C32-C31	177.2(2)
C38-C33-P1-C27	-16.2(2)
C34-C33-P1-Ru1	-64.2(2)
C38-C33-P1-Ru1	118.18(19)
C38-C33-C34-C35	0.5(4)
P1-C33-C34-C35	-177.28(19)
C33-C34-C35-C36	0.7(4)
C34-C35-C36-C37	-1.2(4)
C35-C36-C37-C38	0.5(4)
C36-C37-C38-C33	0.6(4)
C34-C33-C38-C37	-1.1(4)
P1-C33-C38-C37	176.52(19)
P1-C39-C40-P2	54.63(18)
C46-C41-C42-C43	-1.1(4)
P2-C41-C42-C43	173.4(2)
C41-C42-C43-C44	0.8(4)
C42-C43-C44-C45	0.7(4)
C43-C44-C45-C46	-1.9(4)
C44-C45-C46-C41	1.6(4)
C42-C41-C46-C45	0.0(4)
P2-C41-C46-C45	-174.72(19)
C52-C47-C48-C49	2.0(4)
P2-C47-C48-C49	-176.27(18)
C47-C48-C49-C50	-2.0(4)
C48-C49-C50-C51	0.9(4)
C49-C50-C51-C52	0.2(4)
C50-C51-C52-C47	-0.3(4)
C48-C47-C52-C51	-0.8(4)
P2-C47-C52-C51	177.40(19)
O2-C15-O3-C16	-1.9(4)
C5-C15-O3-C16	177.7(2)

C40-C39-P1-C33	-176.19(16)
C40-C39-P1-C27	77.90(17)
C40-C39-P1-Ru1	-46.82(16)
C28-C27-P1-C33	82.6(2)
C32-C27-P1-C33	-95.2(2)
C28-C27-P1-C39	-171.4(2)
C32-C27-P1-C39	10.9(2)
C28-C27-P1-Ru1	-54.2(2)
C32-C27-P1-Ru1	128.07(19)
C42-C41-P2-C47	-110.2(2)
C46-C41-P2-C47	64.3(2)
C42-C41-P2-C40	144.8(2)
C46-C41-P2-C40	-40.7(2)
C42-C41-P2-Ru1	24.7(2)
C46-C41-P2-Ru1	-160.73(17)
C48-C47-P2-C41	50.7(2)
C52-C47-P2-C41	-127.5(2)
C48-C47-P2-C40	157.24(19)
C52-C47-P2-C40	-21.0(2)
C48-C47-P2-Ru1	-81.3(2)
C52-C47-P2-Ru1	100.50(19)
C39-C40-P2-C41	-165.42(16)
C39-C40-P2-C47	92.82(17)
C39-C40-P2-Ru1	-38.52(1)

Figure 4.3. View of **Ru Complex-II** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Chapter 5. Diols as Dienophiles: Bridged Carbocycles *via* Ruthenium(0) Catalyzed Transfer Hydrogenative Cycloadditions of Cyclohexadiene or Norbornadiene*

5.1 Introduction

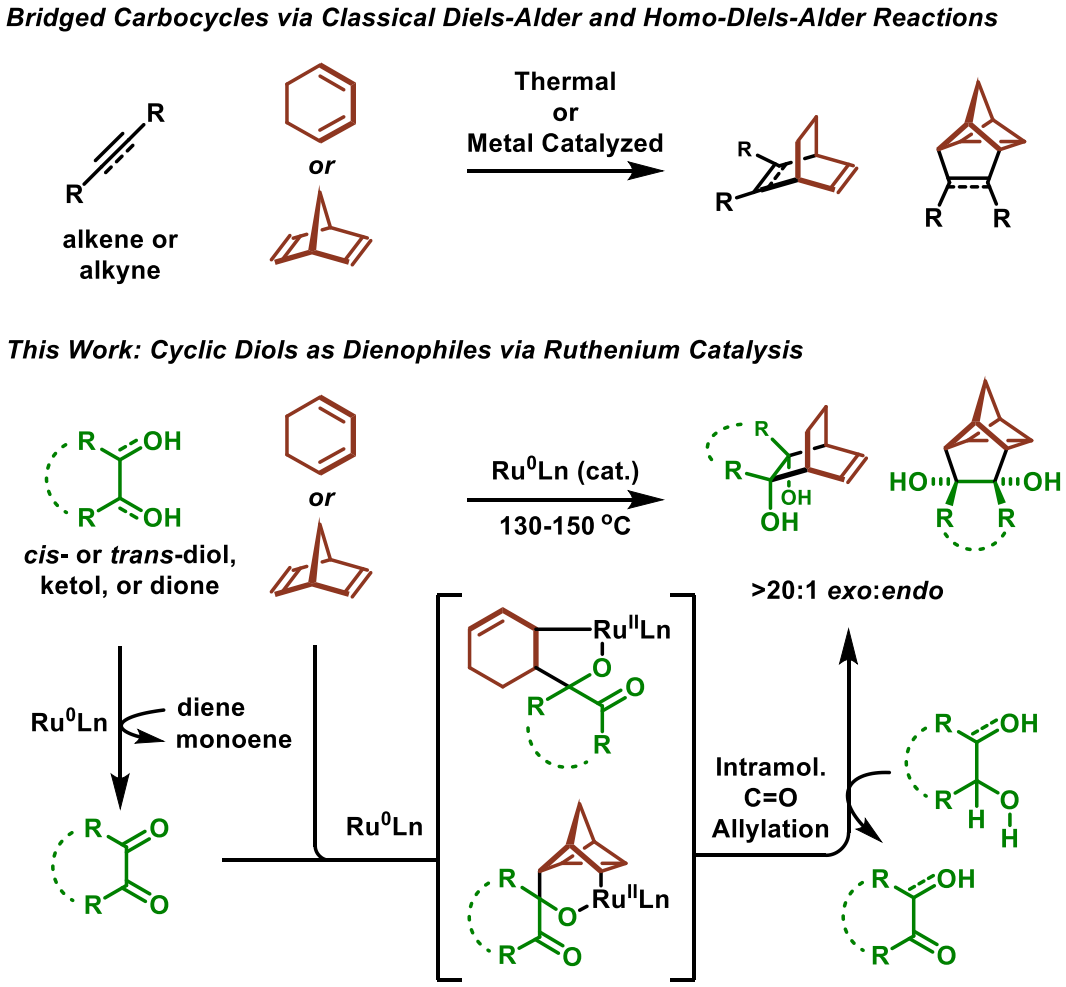


Figure 5.1. Classical Diels-Alder and homo-Diels-Alder cycloadditions to form bridged carbocycles and related transfer hydrogenative variants.

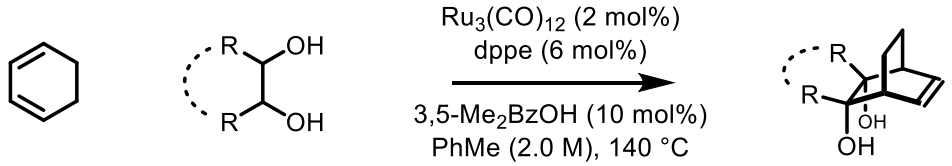
* This chapter is based on the published work:
Sato, H.; Fukaya, K.; Sharma Paudel, B.; Krische, M. J. *Angew. Chem. Int. Ed.* **2017,** *56,* 14667.

Bridged carbocycles are ubiquitous structural motifs in naturally occurring or unnatural bioactive compounds.[1] Transition metal catalyzed cycloaddition reactions[2] are among the most powerful convergent methods to construct complex bridged carbocyclic ring systems. Despite their longstanding history, most of the cycloaddition reactions are limited to a redox-neutral mode, which only allows couplings among unsaturated compounds.[3,4,5] Recently, in the course of the development of catalytic hydrogen transfer reactions,[6,7] we discovered a ruthenium catalyzed redox independent [4+2] cycloaddition of acyclic dienes and diol, ketol or dione.[8,9] In the process, vicinal dicarbonyl derived from diol through dehydrogenation forms a ruthenacycle intermediate.[10] Subsequent intramolecular carbonyl insertion followed by transfer hydrogenolysis affords cyclohexene diol [4+2] cycloadducts. We envisioned that application of this reactivity with cyclic dienes, for examples cyclohexadiene (CHD) and norbornadiene (NBD), would provide a new redox-independent methodology to access bridged carbocycles. However, possible challenges are competing aromatization (CHD to benzene) and catalyst deactivation (Ru-NBD complexes). Herein, we report that cyclohexadiene and norbornadiene readily proceed in the cycloaddition reactions, delivering bridged carbocycles with complete levels of *exo*-selectivity (Figure 5.1). We also demonstrate the redox-independent nature of these processes, which may be conducted from the diol, ketol or dione oxidation levels.

5.2 Results and Discussion

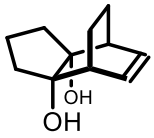
To explore the feasibility of the coupling with cyclic dienes, the reaction of cyclohexadiene **5.1a** (500 mol%) and cyclopentane diol **5.2a** (100 mol%) with ruthenium catalyst derived from $Ru_3(CO)_{12}$ (2 mol%) and various phosphine ligands (12 mol% for monodentate ligands; 6 mol% for chelating ligands) in toluene solvent (2.0 M) at 140 ˚C was conducted. After ligand screening,

Table 5.1. Ruthenium catalyzed cycloaddition of cyclohexadiene 1a with diols **5.2a**-**5.2f** to form bridged bicycles **5.3a**-**5.3f**.[a]

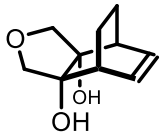


5.1a (500 mol%) **5.2a-f** (100 mol%) **5.3a-f**

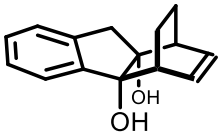
5.2a, 1,2-cyclopentane diol **5.2b**, 3,4-tetrahydrofuran diol **5.2c**, 1,2-dihydroindene diol
5.2d, acenaphthylene diol **5.2e**, H_6-5,6-phthalimide diol **5.2f**, 1,2-propane diol



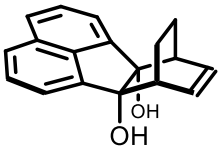
5.3a, 95% Yield
>20:1 dr



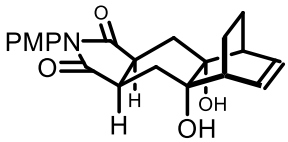
5.3b, 99% Yield
>20:1 dr (**X-Ray**)



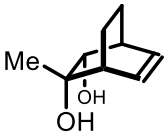
5.3c, 81% Yield[b]
>20:1 dr



5.3d, 85% Yield
>20:1 dr



5.3e, 91% Yield[c]
>20:1 dr (**X-Ray**)



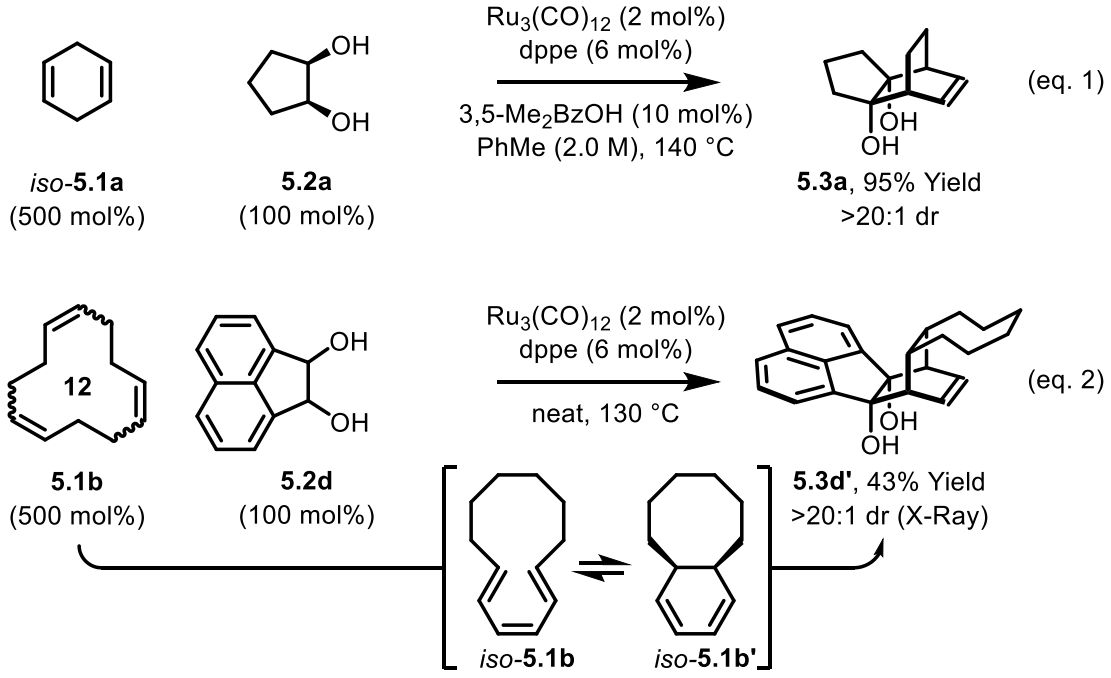
5.3f, 58% Yield[d]
>20:1 dr

[a]Yields are of material isolated by silica gel chromatography. [b]rac-BINAP (6 mol%) [c]Without 3,5-Me_2BzOH, 150 °C. [d]dCype (6 mol%). The ketol dehydro-**5.3f** was formed in 13% yield. See Supporting Information for further experimental details.

the ruthenium(0) catalyst modified by bis(diphenylphosphino)ethane (dppe) delivered the hydroxy substituted bridged bicycle **5.3a** in 77% yield with complete levels of *exo*- and *cis*- diol selectivity. Aforementioned (Figure 5.1), our collective studies on the ruthenium(0) catalyzed C-C coupling of alcohols[6c] are consistent with catalytic mechanisms involving diene-dione oxidative coupling to form oxaruthenacycles.[10] Carboxylic acid additives are known to accelerate the hydrogenolysis[11] and transfer hydrogenolysis[12] of oxa- and azametallacycles. Therefore, carboxylic acid additives were able to improve the turn over number by promoting these steps. To

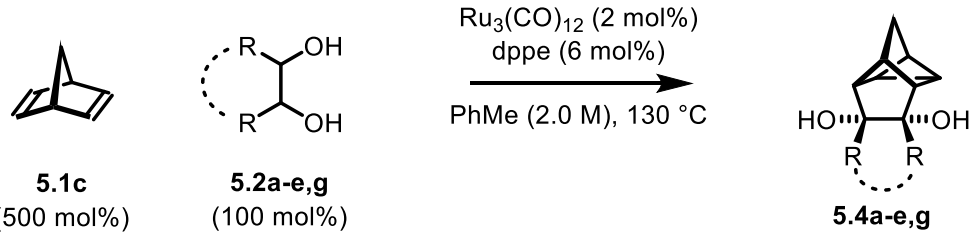
our delight, in the presence of 3,5-dimethylbenzoic acid (10 mol%), the bicyclic product of [4+2] cycloaddition **5.3a** was obtained in 95% yield. To explore the generality of diols, cyclohexadiene was reacted with various cyclic diols **5.2a**-**5.2e** to give the corresponding [4+2] cycloadducts **5.3a**-**5.3e** in good yield with complete *exo*-selectivity (Table 5.1). Acyclic diol **5.2f** was also incorporated in cycloaddition to form adduct **5.3f** as a single diastereomer, along with a small quantitiy of the ketol *dehydro*-**5.3f**. The stereochemistry of the diol substrates did not affect the cycloaddition reactions. The dihydride complex $H_2Ru(CO)(PPh_3)_3$ (6 mol%) instead of $Ru_3(CO)_{12}$ also catalyzed the cycloaddition of cyclohexadiene **5.1a** with cyclopentane diol **5.2a** to form **5.3a** in 93% yield.

The ability of $Ru_3(CO)_{12}$ to catalyze olefin isomerization[13] enables the cycloaddition reactions to engage non-conjugated dienes. Exposure of 1,4-cyclohexadiene *iso*-**5.1a** and cyclopentane diol **5.2a** under the standard reaction conditions gave the bridged bicycle **5.3a** in



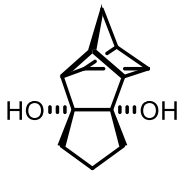
Scheme 5.1. Cycloaddition reactions via isomerization and tandem reactions from iso-**5.1a** to **5.3a** (eq. 1) and from **5.1b** to **5.3d`** (eq. 2).

Table 5.2. Ruthenium catalyzed cycloaddition of norbornadiene **5.1c** with diols **5.2a-5.2e, 5.2g** to form bridged bicycles **5.4a-5.4e, 5.4g.**[a]

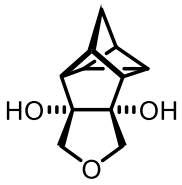


5.1c (500 mol%) | **5.2a-e,g** (100 mol%) | **5.4a-e,g**

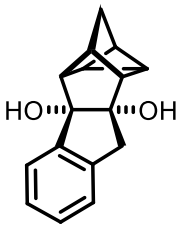
5.2a, 1,2-cyclopentane diol	**5.2b**, 3,4-tetrahydrofuran diol	**5.2c**, 1,2-dihydroindene diol
5.2d, acenaphthylene diol	**5.2e**, H_6-5,6-phthalimide diol	**5.2g**, 1,2-cyclohexane diol



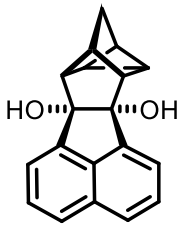
5.4a, 80% Yield
>20:1 dr



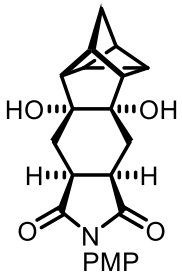
5.4b, 63% Yield[b]
>20:1 dr



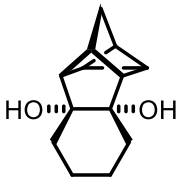
5.4c, 82% Yield
>20:1 dr (**X-Ray**)



5.4d, 91% Yield
>20:1 dr (**X-Ray**)



5.4e, 85% Yield
>20:1 dr (**X-Ray**)



5.4g
54% Yield (from diol **5.2g**)
62% Yield (from ketol *dehydro*-**5.2g**)
>20:1 dr

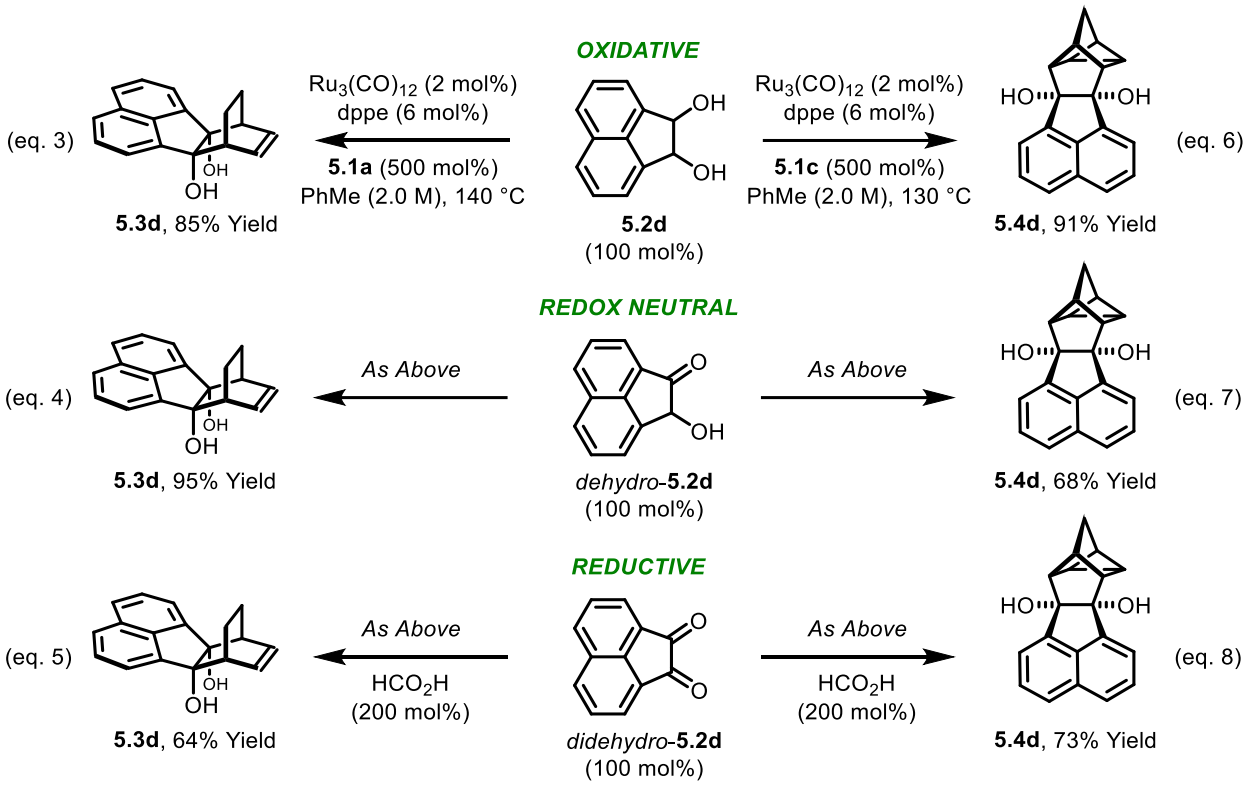
[a]Yields are of material isolated by silica gel chromatography. [b]dppb (6 mol%), 150 °C, dioxane (2.0 M). See Supporting Information for further experimental details.

95% yield, which is similarly efficient when starting with 1,3-cyclohexadiene (Scheme 5.1, eq. 1). An even more powerful application of tandem olefin isomerization-cycloaddition is found in the reaction of 1,5,9-cyclododecatriene **5.1b** with diol **5.2d** to form polycycloadduct **5.3d′** (Scheme 5.1, eq. 2). Here, olefin isomerization results in the generation of a conjugated triene *iso*-**5.1b**, which exists in equilibrium with the corresponding [6.4.0] tricycle *iso*-**5.1b′** through

electrocyclization.[14] Ruthenium(0) catalyzed cycloaddition with the [6.4.0] tricycle provides cycloadduct **5.3d′** as a single diastereomer confirmed by X-ray analysis.

The *homo*-Diels-Alder reaction is a unique and longstanding cycloaddition reaction, wherein norbornadiene **5.1c** and other unsaturated compounds such as alkene or alkyne delivers [2+2+2] polycyclic compounds.[15,16] Motivated by these precedents and the utility of *homo*-Diels-Alder cycloadducts with respect to the synthesis of diquinanes,[17] the ruthenium(0) catalyzed cycloaddition of norbornadiene **5.1c** with cyclopentane diol **5.2a** was explored. To our delight, the product of cycloaddition **5.4a** was formed in 80% yield with complete *exo*- and *cis*-diol diastereoselectivity at 130 ˚C under the conditions used in the [4+2] cycloaddition reaction. The generality of the diol scope was explored with cyclic diols **5.2a**-**5.2e** and **5.2g** (Table 5.2). Unlike cyclohexadiene **5.1a**, norbornadiene **5.1c** did not engage in efficient coupling with acyclic diols. The other ruthenium catalyst source $H_2Ru(CO)(PPh_3)_3$ (6 mol%) also catalyzed the cycloaddition of norbornadiene **5.1c** with cyclopentane diol **5.2a** to form **5.4a** in 67% yield.

While the diol-mediated cycloadditions are oxidative processes in which one equivalent of diene **5.1a**-**5.1c** is required as a sacrificial hydrogen acceptor, the reactions of dienes **5.1a** and **5.1c** with ketol *dehydro*-**5.2d** (Scheme 5.2, eq. 4 and 7) or dione *didehydro*-**5.2d** (Scheme 5.2, eq. 5 and 8), redox-neutral and reductive cycloaddition respectively also provide the identical cycloadduct. As redox-neutral cycloadditions do not need a sacrificial oxidant or reductant, stoichiometric byproducts are avoided. Reductive cycloadditions with formic acid (200 mol%) as hydrogen donor also employs the desired cycloadduct, which expands the substrate scopes of this reaction.

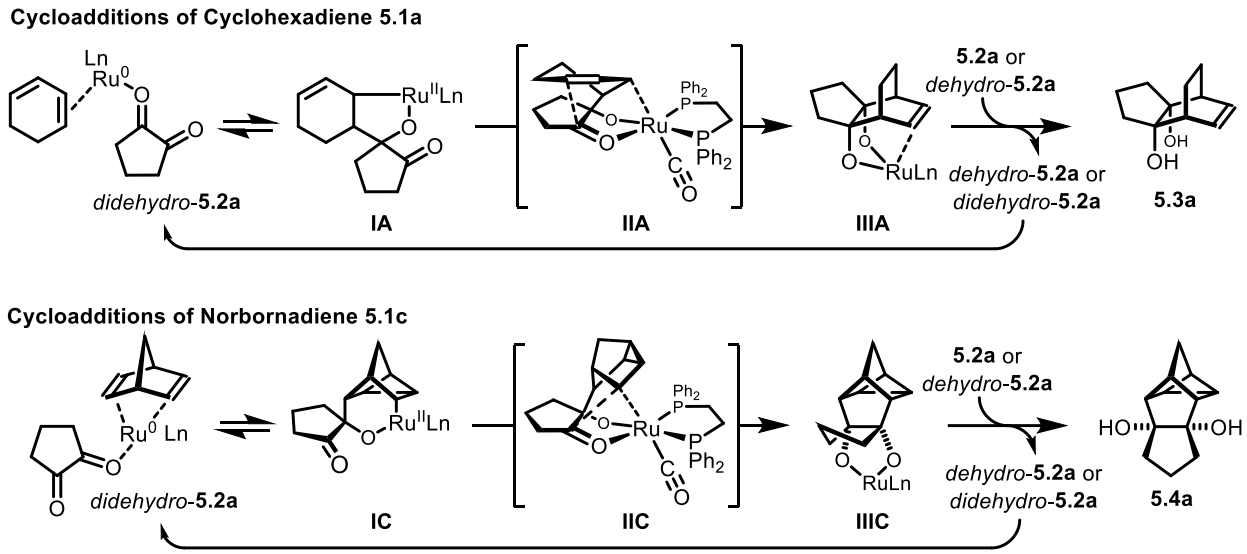


Scheme 5.2. Redox level independent cycloaddition of cyclohexadiene **5.1a** and norbornadiene **5.1c** with diol **5.2d**, ketol dehydro-**5.2d** and dione didehydro-**5.2d**.[a]

[a] Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

5.3 Mechanism

A mechanism and stereochemical model accounting for *exo*- and *cis*-diol selectivity is proposed, as illustrated in couplings of cyclohexadiene **5.1a** and norbornadiene **5.1c** with diol **5.2a** (Scheme 5.3). The cycloaddition begins with dehydrogenation of diol **5.2a** to the dione *didehydro*-**5.2a**.[18-20] Reversible[10] ruthenium(0)-mediated oxidative coupling of dione *didehydro*-**5.2a** to cyclohexadiene **5.1a** or norbornadiene **5.1c** delivers oxa-ruthenacycles **IA** and **IC**, respectively.[21,22] The second C-C bond formation via intramolecular carbonyl addition occurs in the transient **IIA** and **IIC** to produce **IIIA** and **IIIC** intermediate. Finally, transfer hydrogenolytic cleavage of the metallacycle with diol **5.2a** or ketol *dehydro*-**5.2a** releases the cycloadducts **5.3a**



Scheme 5.3. General mechanism and stereochemical model accounting for *exo*-selectivity.

and **5.4a**. The carboxylic acid cocatalyst is thought to accelerate transfer hydrogenolysis of the sterically congested metalacycle **IIIA** *via* protonolytic cleavage (not shown).[12b] An attempt to 3 component cycloaddition with carbon monoxide as reported by Kondo[23] group under similar conditions proved ineffective. The reaction of cyclopentanediol with cyclohexadiene **5.1a** or norbornadiene **5.1c** under carbon monoxide pressure did not give any carbon monoxide incorporated cycloadducts. Finally, whereas the carbonyl complex $H_2Ru(CO)(PPh_3)_3$ is capable of catalyzing the present diol-mediated cycloadditions of cyclohexadiene **5.1a** and norbornadiene **5.1c**, the related complex lacking a carbonyl ligand, $H_2Ru(PPh_3)_4$, is inactive. A carbonyl ligand may be required to facilitate alkoxide exchange at ruthenium by way of an acylruthenium intermediate.[24]

5.4 Summary

In summary, we report highly *exo*- and *cis*-diol selective ruthenium(0) catalyzed transfer hydrogenative cycloadditions of cyclohexadiene **5.1a** or norbornadiene **5.1c** with 1,2-diols **5.2a**-

5.2g to form bridged carbocycles. Distinctively, these transformations proceed in a redox-independent manner, which allows the use of diol, ketol or dione oxidation levels. Also, the ability of ruthenium catalyst to isomerize olefins were able to engage non-conjugated dienes. These processes contribute to the growing class of transfer hydrogenative cycloadditions[8,9] and expand the scope of novel cycloadducts which were difficult to access by conventional cycloaddition methodologies.

5.5 Experimental Details

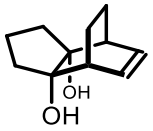
General Comments

All glassware was oven dried at 120 ˚C overnight and cooled in a desiccator. All ruthenium catalyzed reactions were carried in sealed pressure tubes (13 x 100 mm). THF was purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], dppe, dCype, *rac*-BINAP, dppb, 3,5-dimethylbenzoic acid, dienes **5.1a**, *iso*-**5.1a**, triene **5.1b** and norbornadiene **5.1c** were purchased from commercial suppliers and used as received. Diols **5.2a**, **5.2f** and **5.2g** were purchased from commercially available sources and used without purification. **5.2b**,[25] **5.2c**,[26] **5.2d**[27] and **5.2e**[28] were prepared according to previous literature. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded with a Bruker AVANCE III (500 MHz supported by NSF grant 1 S10 OD021508-01) spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on Agilent Technologies 6530 Accurate-Mass Q-TOF and are reported as m/z. Masses are reported for the molecular ion (M-H, M, M+H or M+Na).

General Procedure and Spectral Data for Cycloaddition Reactions with Cyclohexadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), 3,5-Me_2BzOH (4.5 mg, 0.03 mmol, 10 mol%), diol (0.3 mmol, 100 mol%) and 1,3 cyclohexadiene (1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 140 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **5.3a-5.3f**.

(3a*RS*,4*SR*,7*RS*,7a*SR*)-2,3,4,7-tetrahydro-1*H*-4,7-ethanoindene-3a,7a-diol (5.3a)



The reaction was conducted with *cis*-cyclopentane-1,2-diol **5.2a** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 25:75) provided the title compound **5.3a** (51.2 mg, 0.29 mmol) in 95% yield as a white solid.

TLC (SiO_2): R_f = 0.30 (AcOEt:hexanes = 3:7).

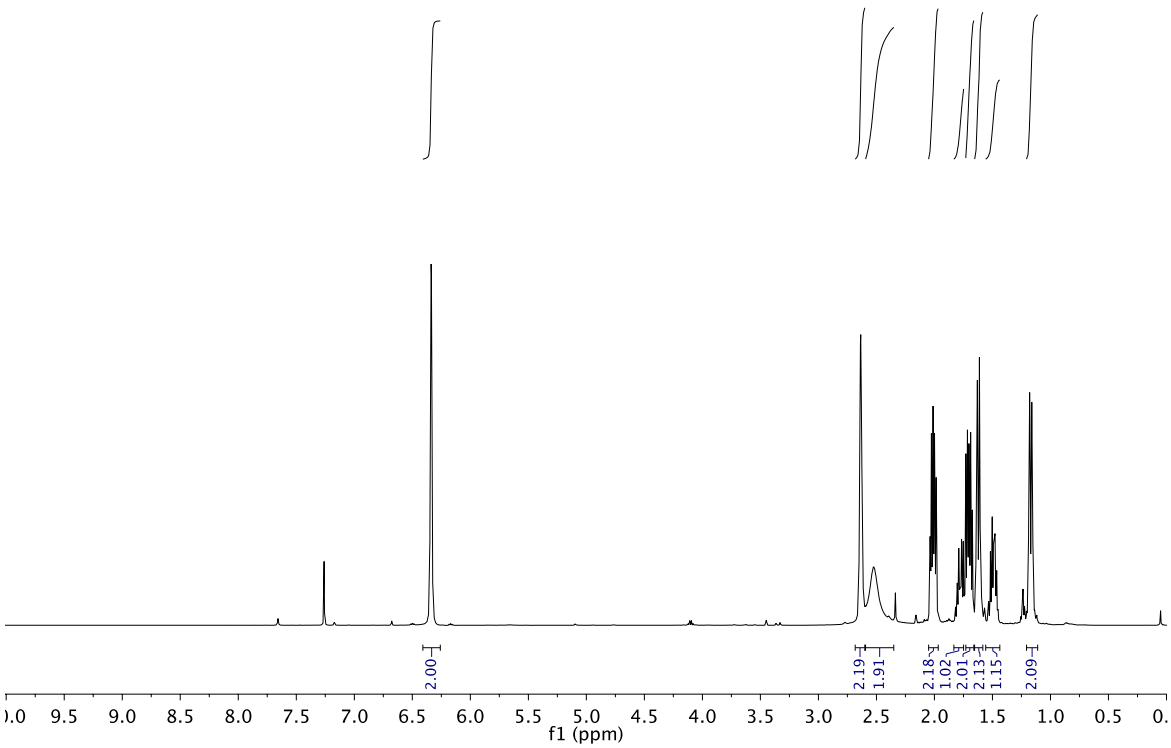
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 6.34 (dd, 4.5, 3.0 Hz, 2H), 2.64 (dt, *J* = 5.1, 2.7 Hz, 2H), 2.59 - 2.35 (m, 2H), 2.05 - 1.97 (m, 2H), 1.83 - 1.75 (m, 1H), 1.70 (dt, *J* = 14.6, 7.4 Hz, 2H), 1.65 - 1.58 (m, 2H), 1.49 (m, 1H), 1.21 - 1.11 (m, 2H) ppm.

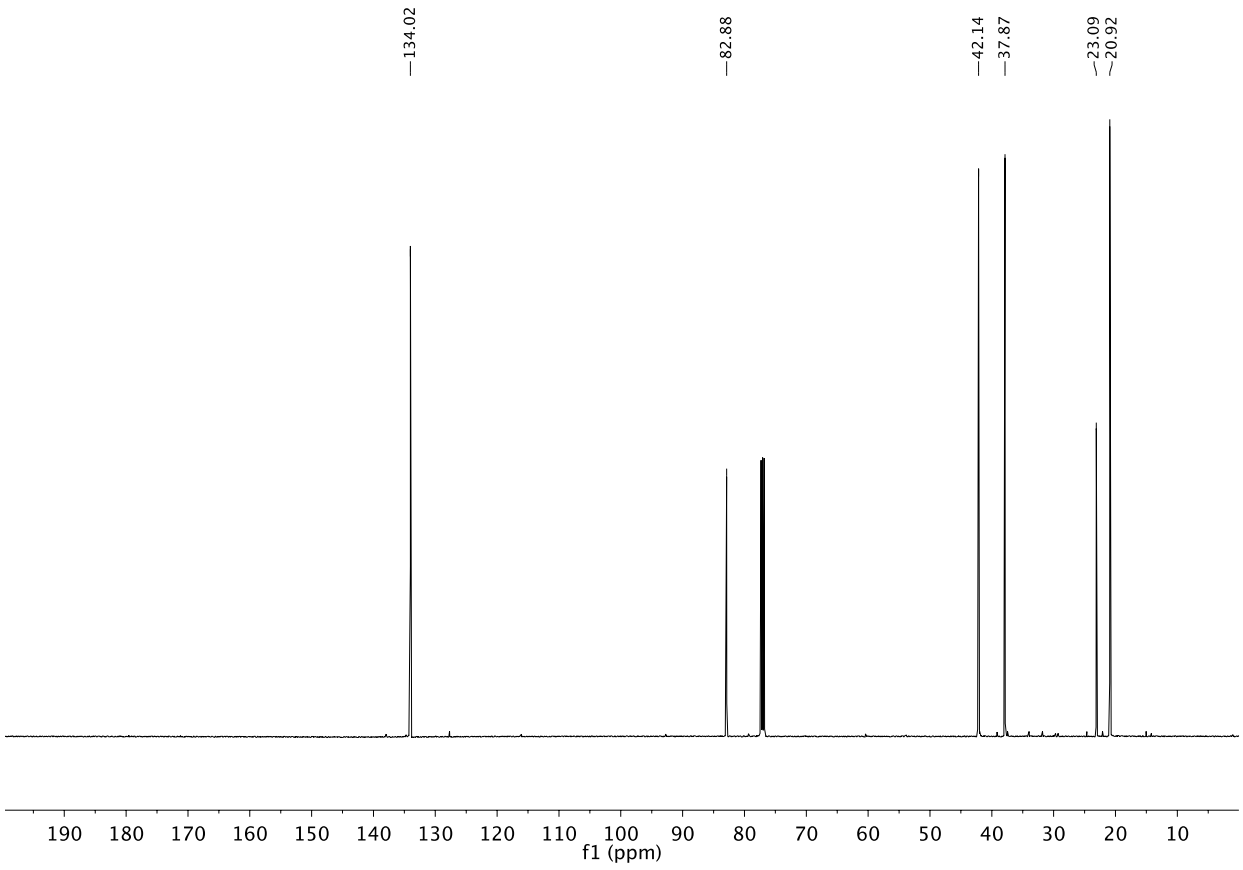
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 134.0, 82.9, 42.1, 37.9, 23.1, 20.9 ppm.

MP: 106.5-110.8 °C.

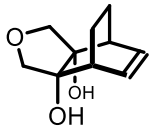
HRMS: (ESI) Calculated for $C_{11}H_{16}O_2Na$ [M+Na^+] = 203.1043, Found 203.1041.

FTIR: (neat): 2970, 2363, 2342, 1738 cm^{-1}.


2.00
2.19
1.91
2.18
1.02
2.01
2.13
1.15
2.09
f1 (ppm)


134.02
82.88
42.14
37.87
23.09
20.92
f1 (ppm)

(3a*RS*,4*RS*,7*SR*,7a*SR*)-4,7-dihydro-4,7-ethanoisobenzofuran-3a,7a(1*H*,3*H*)-diol (5.3b)



The reaction was conducted with *cis*-3,4-tetrahydrofuran diol **5.2b** in accordance with the general procedure. Flash column chromatography (AcOEt:hexanes = 80:20) provided the title compound **5.3b** (54.1 mg, 0.30 mmol) in 99% yield as a white solid.

TLC (SiO_2): R_f = 0.45 (AcOEt:hexanes = 8:2).

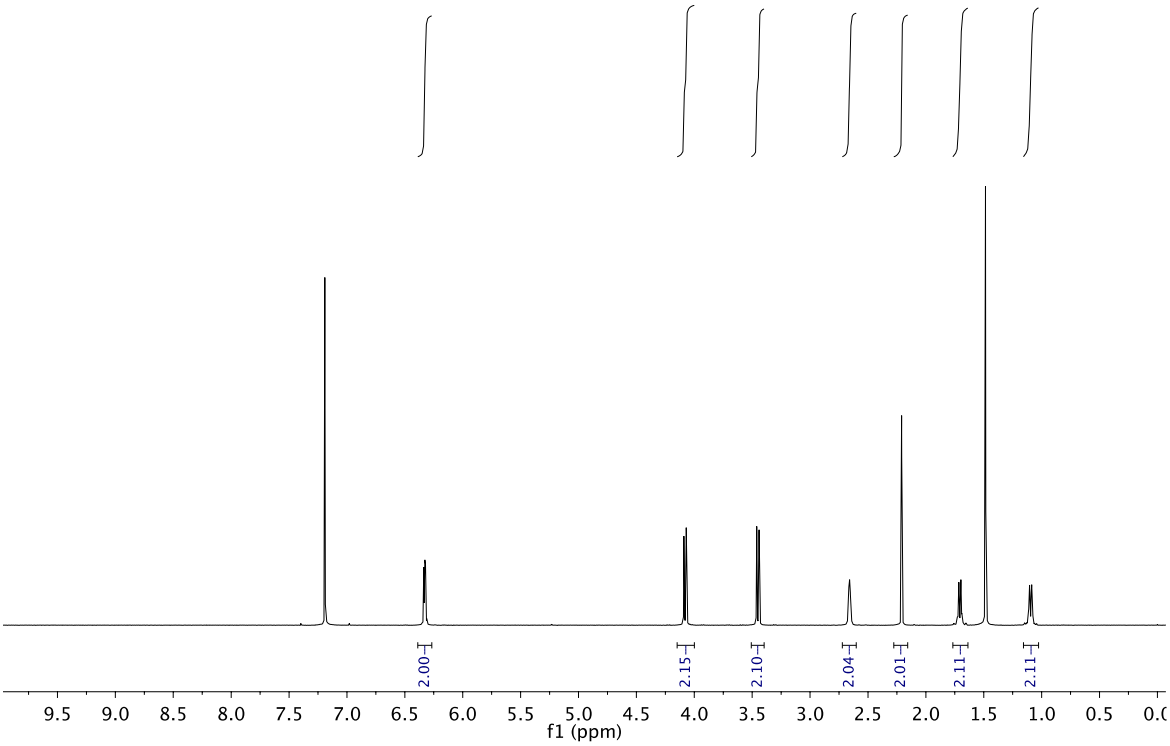
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 6.33 (dd, *J* = 4.5, 3.0 Hz, 2H), 4.08 (d, *J* = 10.0 Hz, 2H), 3.45 (d, *J* = 10.0 Hz, 2H), 2.66 (dt, *J* = 4.6, 2.7 Hz, 2H), 2.21 (s, 2H), 1.77 - 1.64 (m, 2H), 1.16 - 1.03 (m, 2H) ppm.

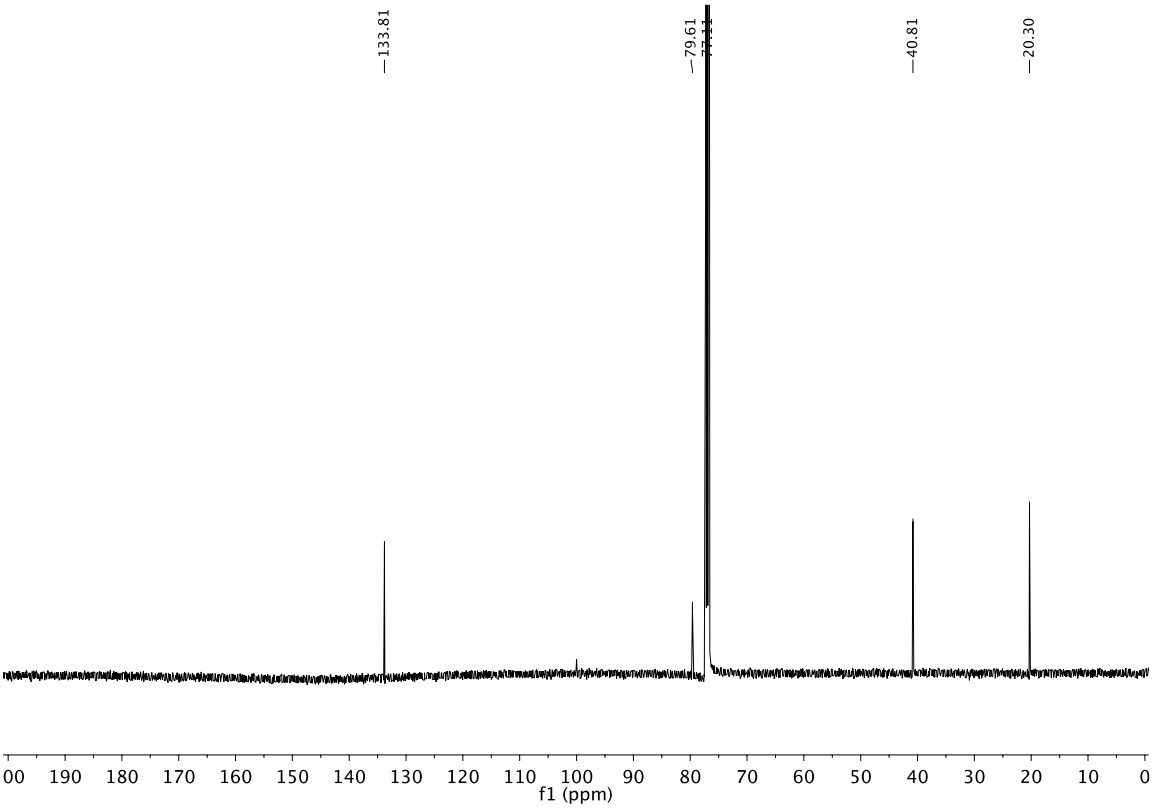
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 133.8, 79.6, 77.1, 40.8, 20.3 ppm.

MP: decomposed at 240 °C.

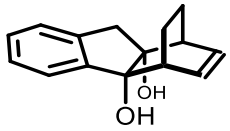
HRMS: (ESI) Calculated for $C_{10}H_{14}O_3Na$ [M+Na^+] = 205.0835, Found 2085.0836.

FTIR: (neat): 3400, 2869, 2364 cm^{-1}.


2.00
2.15
2.10
2.04
2.01
2.11
2.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


133.81
79.61
77.41
40.81
20.30
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(1*RS*,4*SR*,4a*SR*,9a*SR*)-1,4-dihydro-4a*H*-1,4-ethanofluorene-4a,9a(9*H*)-diol (5.3c)



The reaction was conducted with mixture of *trans*- and *cis*- 1,2-dihydroindenediol **5.2c** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 20:80) provided the title compound **5.3c** (55.5 mg, 0.24 mmol) in 81% yield as a white solid.

TLC (SiO_2): R_f = 0.30 (AcOEt:hexanes = 3:7).

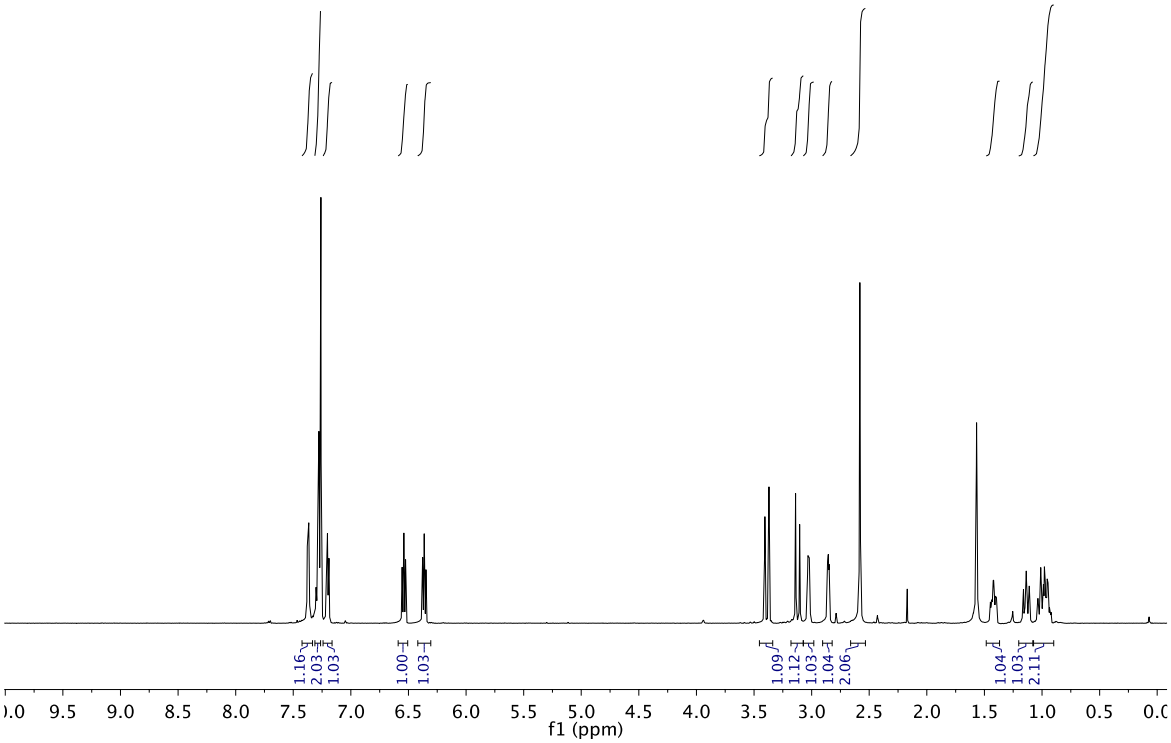
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.28 (td, *J* = 5.8, 5.1, 2.6 Hz, 2H), 7.20 (dd, *J* = 7.3, 1.7 Hz, 1H), 6.54 (ddd, *J* = 7.7, 6.3, 1.1 Hz, 1H), 6.36 (dd, *J* = 7.9, 6.5 Hz, 1H), 3.39 (d, *J* = 17.8 Hz, 1H), 3.12 (d, J = 17.8 Hz, 1H), 3.03 (dt, *J* = 6.5, 2.9 Hz, 1H), 2.86 (dt, *J* = 5.1, 2.1 Hz, 1H), 2.58 (s, 2H), 1.42 (dddd, *J* = 13.7, 9.5, 4.7, 2.1 Hz, 1H), 1.14 (ddt, *J* = 13.4, 11.6, 4.1 Hz, 1H), 1.07 - 0.90 (m, 2H).

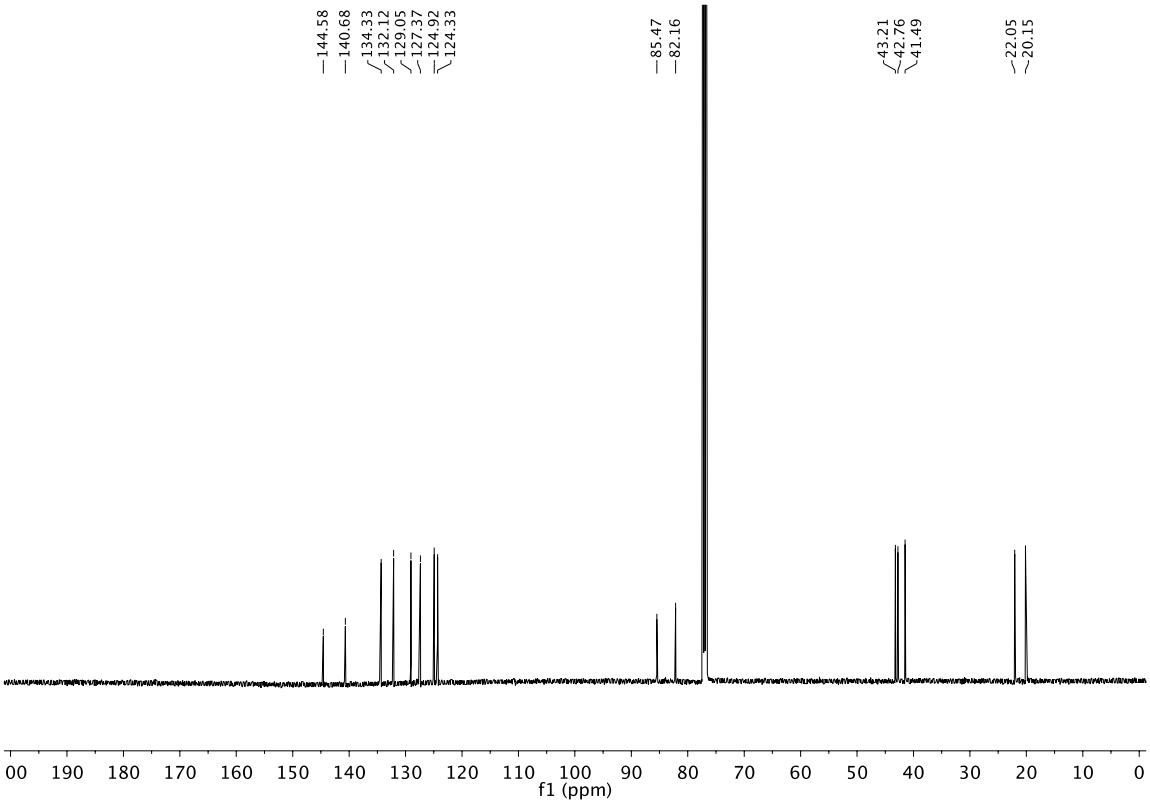
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 144.6, 140.7, 134.3, 132.1, 129.1, 127.4, 124.9, 124.3, 85.5, 82.2, 43.2, 42.8, 41.5, 22.1, 20.2 ppm.

MP: 114.2-116.8 °C.

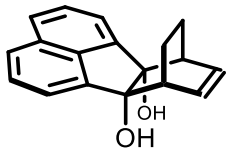
HRMS: (ESI) Calculated for $C_{15}H_{16}O_2Na$ [M+Na^+] = 251.1043, Found 251.1044.

FTIR: (neat): 3304, 2947, 2364, 1739 cm^{-1}.


1.16
2.03
1.03
1.00
1.03
1.09
1.12
1.03
1.04
2.06
1.04
1.03
2.11
f1 (ppm)


144.58
140.68
134.33
132.12
129.05
127.37
124.92
124.33
85.47
82.16
43.21
42.76
41.49
22.05
20.15
f1 (ppm)

(6b*RS*,7*RS*,10*SR*,10a*SR*)-7,10-dihydro-7,10-ethanofluoranthene-6b,10a-diol (5.3d)



The reaction was conducted with mixture of *trans*- and *cis*- acenaphthylene diol **5.2d** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 15:85) provided the title compound **5.3d** (67.5 mg, 0.26 mmol) in 85% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (AcOEt:hexanes = 3:7).

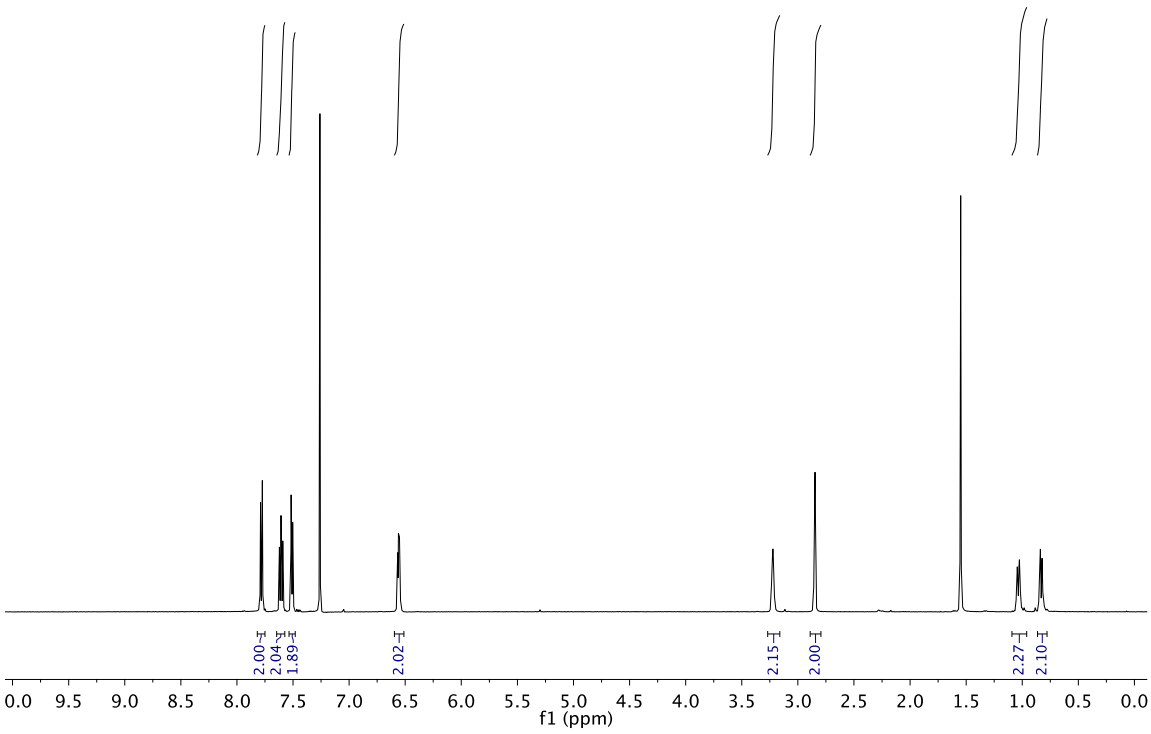
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 6.56 (dt, *J* = 5.7, 2.9 Hz, 2H), 3.22 (dt, *J* = 5.3, 2.8 Hz, 2H), 2.85 (d, *J* = 1.3 Hz, 2H), 1.09 - 0.96 (m, 2H), 0.86 - 0.78 (m, 2H) ppm.

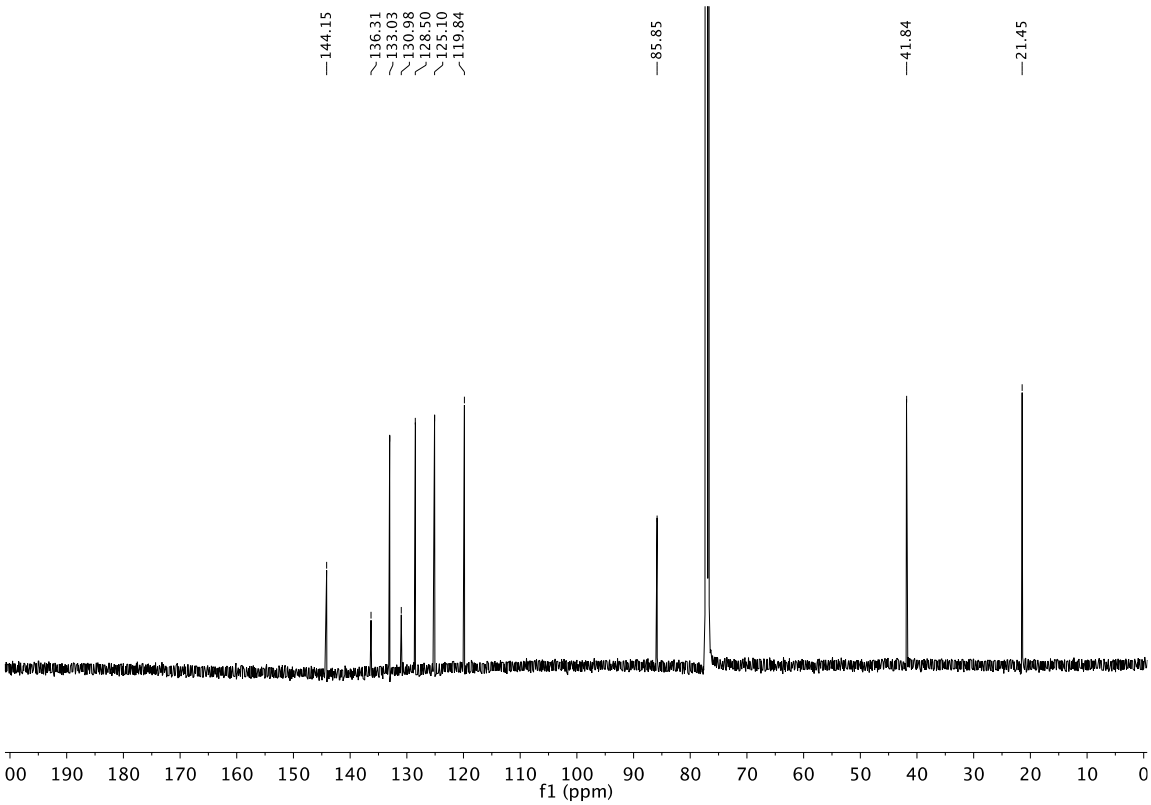
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 144.2, 136.3, 133.0, 131.0, 128.5, 125.1, 119.8, 85.9, 41.8, 21.5 ppm.

MP: 195.5-197.0 °C.

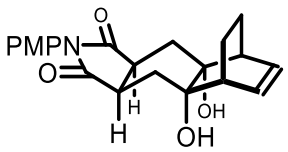
HRMS: (ESI) Calculated for $C_{18}H_{16}O_2Na$ [M+Na^+] = 287.1043, Found 287.1047.

FTIR: (neat): 3410, 2365, 1739 cm^{-1}.


2.00
2.04
1.89
2.02
2.15
2.00
2.27
2.10
f1 (ppm)


144.15
136.31
133.03
130.98
128.50
125.10
119.84
85.85
41.84
21.45
f1 (ppm)

(3a*RS*,4a*SR*,5*RS*,8*SR*,8a*RS*,9a*SR*)-4a,8a-dihydroxy-2-(4-methoxyphenyl)-3a,4,4a,5,8,8a,9,9a-octahydro-1*H*-5,8-ethanobenzo[*f*]isoindole-1,3(2*H*)-dione (5.3e)



The reaction was conducted with (3a*RS*,5*RS*,6*SR*,7a*SR*)-5,6-phthalimide diol **5.2e** without 3,5-Me_2BzOH at 150 ˚C. Flash column chromatography (SiO_2, AcOEt:hexanes = 70:30) provided the title compound **5.3e** (99.6 mg, 0.27 mmol) in 91% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (AcOEt:hexanes = 8:2).

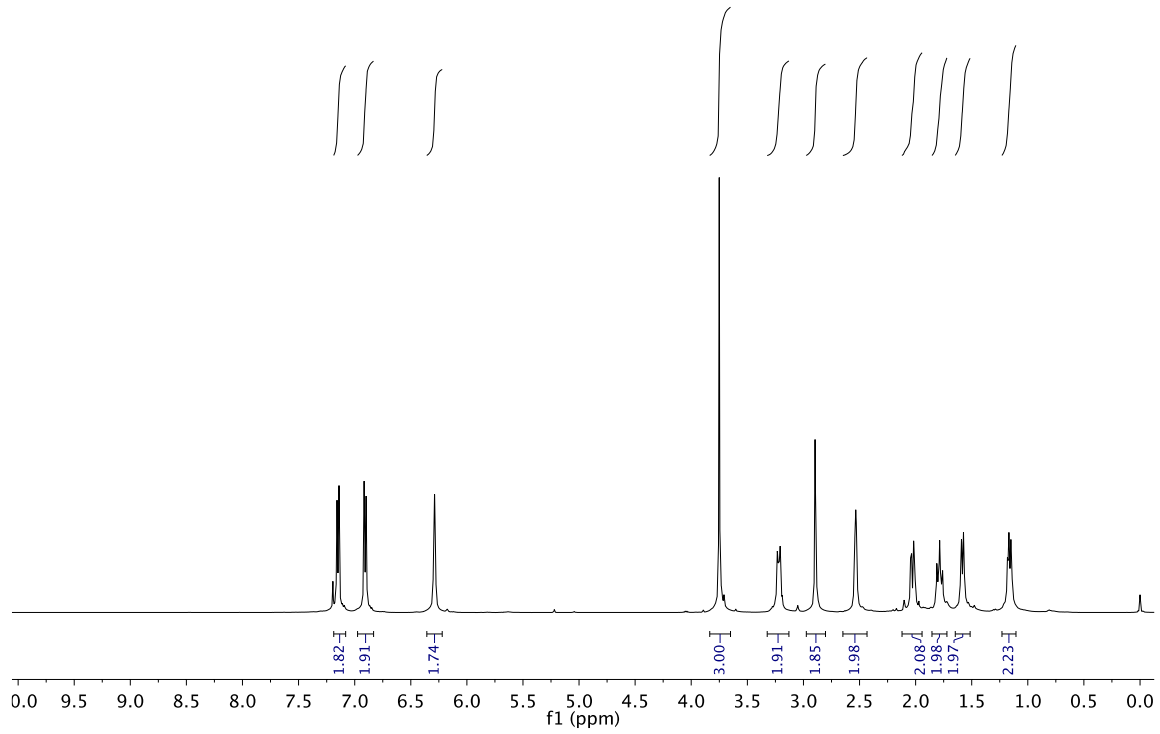
^{1}H NMR: (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.29 (t, *J* = 3.8 Hz, 2H), 3.75 (s, 3H), 3.23 (m, 2H), 2.90 (s, 2H), 2.53 (d, *J* = 4.2 Hz, 2H), 2.12 - 1.94 (m, 2H), 1.79 (t, *J* = 12.8 Hz, 2H), 1.58 (t, *J* = 7.7 Hz, 2H), 1.23 - 1.11 (m, 2H) ppm.

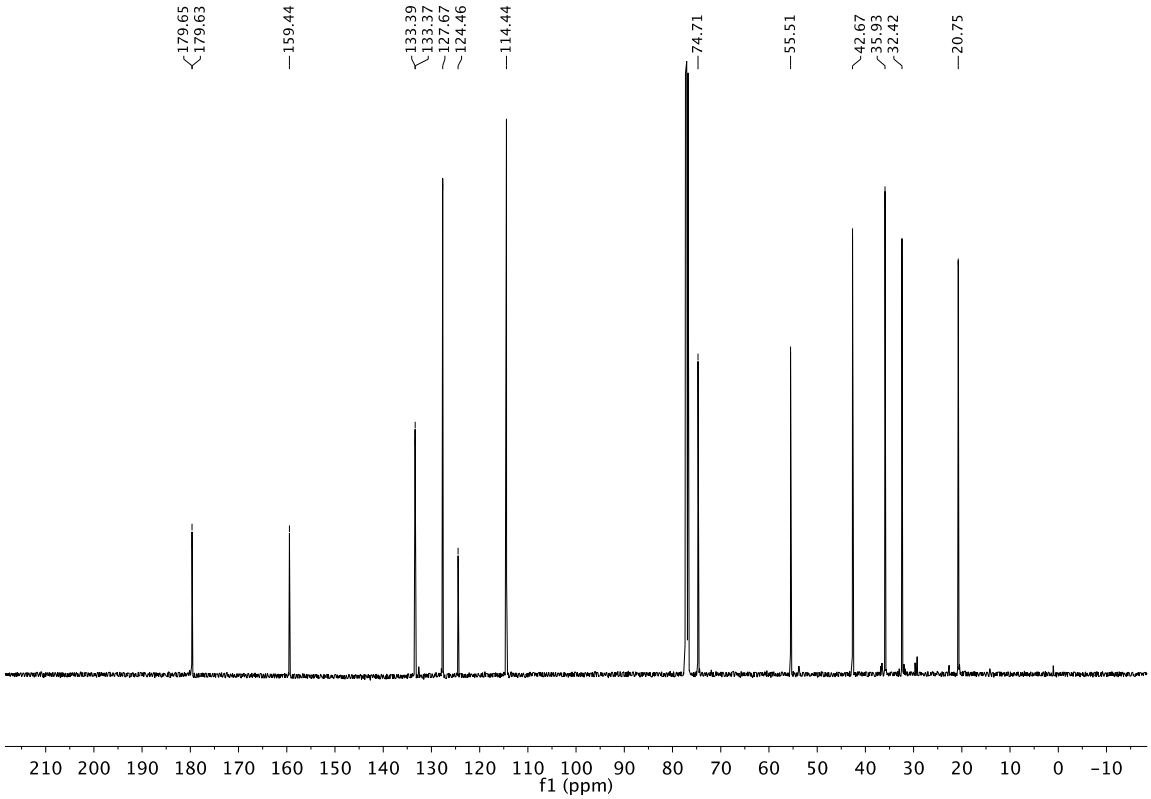
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 179.7, 179.6, 159.4, 133.4, 133.4, 127.7, 124.5, 114.4, 74.7, 55.5, 42.7, 35.9, 32.4, 20.8 ppm.

MP: 230.6-240.2 °C.

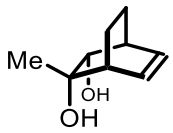
HRMS: (ESI) Calculated for $C_{21}H_{32}O_5Na$ [M+Na^+] =392.1468, Found 392.1468.

FTIR: (neat): 3487, 2946, 2364, 1693, 1514 cm^{-1}.


1.82
1.91
1.74
3.00
1.91
1.85
1.98
2.08
1.98
1.97
2.23
f1 (ppm)


179.65
179.63
159.44
133.39
133.37
127.67
124.46
114.44
74.71
55.51
42.67
35.93
32.42
20.75
f1 (ppm)

(1*RS*,2*SR*,3*RS*,4*SR*)-2-methylbicyclo[2.2.2]oct-5-ene-2,3-diol (5.3f)



The reaction was conducted with 1,2-propanediol **5.2f** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 30:70) provided **S5.1** (5.5 mg, 0.04 mmol) in 13% as yellow liquid, and (AcOEt:hexanes = 60:40) the title compound **5.3f** (26.8 mg, 0.17 mmol) in 58% yield as slightly yellow liquid.

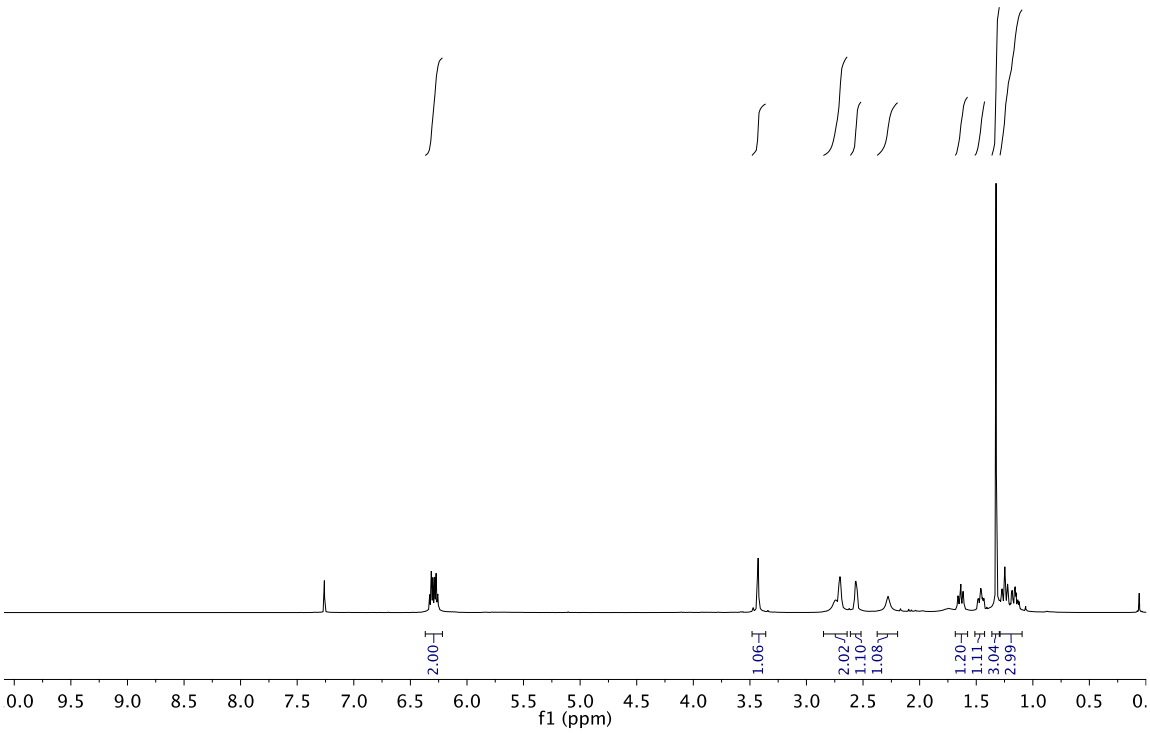
TLC (SiO_2): R_f = 0.45 (AcOEt:hexanes = 8:2).

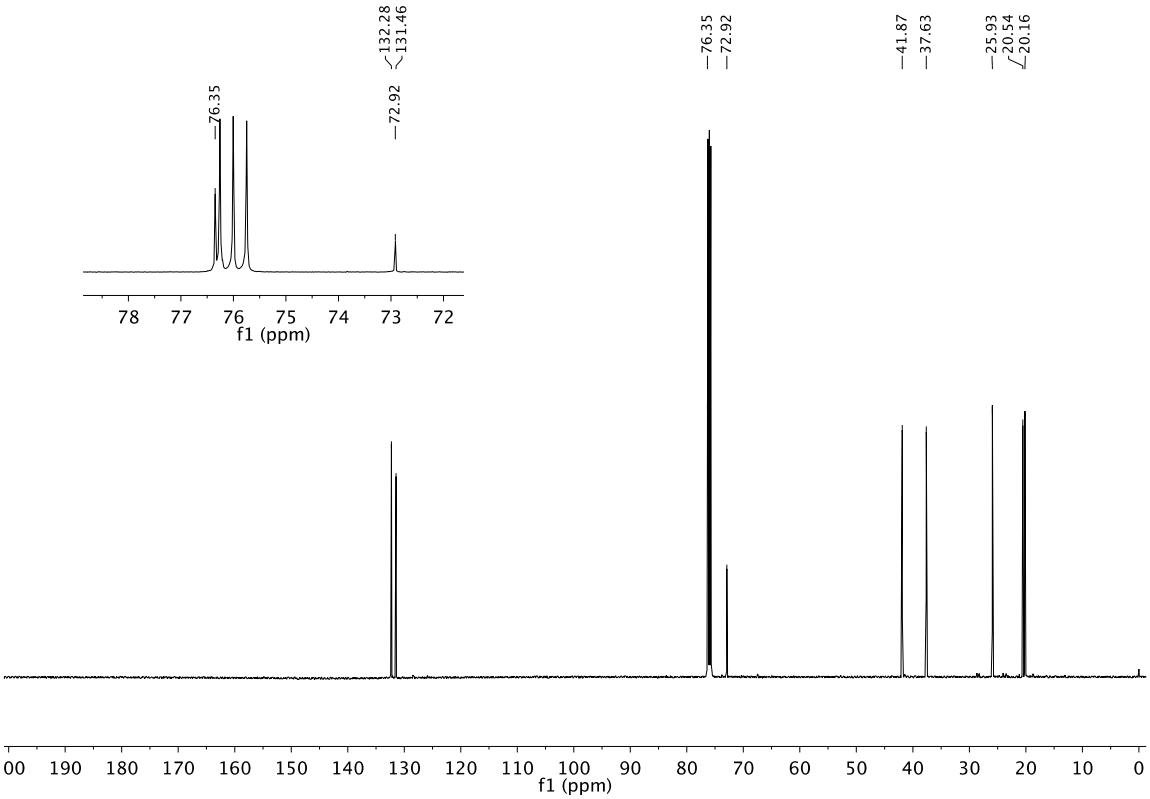
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 6.37 - 6.22 (m, 2H), 3.43 (d, *J* = 2.7 Hz, 1H), 2.85 - 2.64 (m, 2H), 2.61 - 2.52 (m, 1H), 2.28 (s, 1H), 1.64 (ddt, *J* = 13.0, 9.9, 3.1 Hz, 1H), 1.46 (dddd, *J* = 11.7, 9.3, 4.8, 2.1 Hz, 1H), 1.32 (s, 3H), 1.29 - 1.09 (m, 3H) ppm

^{13}C NMR: (125 MHz, $CDCl_3$): δ = 132.3, 131.5, 76.4, 72.9, 41.9, 37.6, 25.9, 20.5, 20.2 ppm.

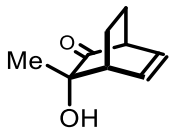
HRMS: (ESI) Calculated for $C_9H_{14}O_2Na$ [M+Na^+] =177.0886, Found 177.0888.

FTIR: (neat): 3360, 2949 cm^{-1}.


2.00
1.06
2.02
1.10
1.08
1.20
1.11
3.04
2.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


132.28
131.46
76.35
72.92
41.87
37.63
25.93
20.54
20.16
78 77 76 75 74 73 72
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(1*SR*,3*SR*,4*RS*)-3-hydroxy-3-methylbicyclo[2.2.2]oct-5-en-2-one (S5.1)



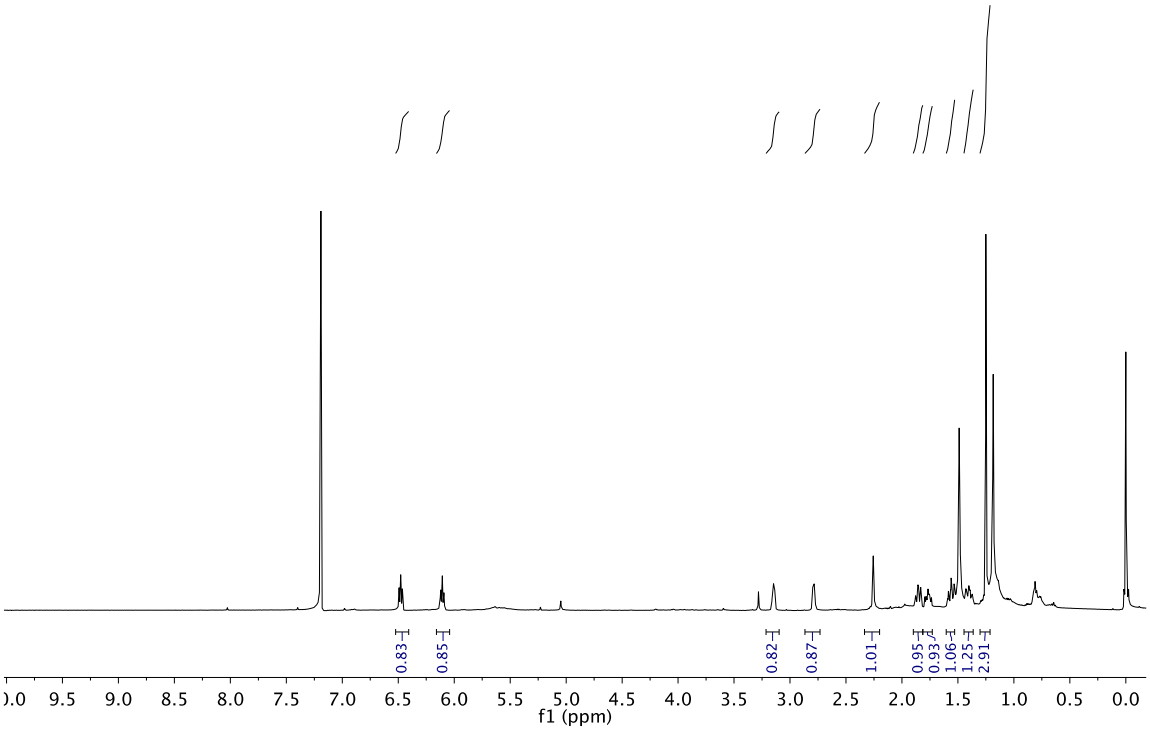
TLC (SiO_2): R_f = 0.25 (AcOEt:hexanes = 3:7).

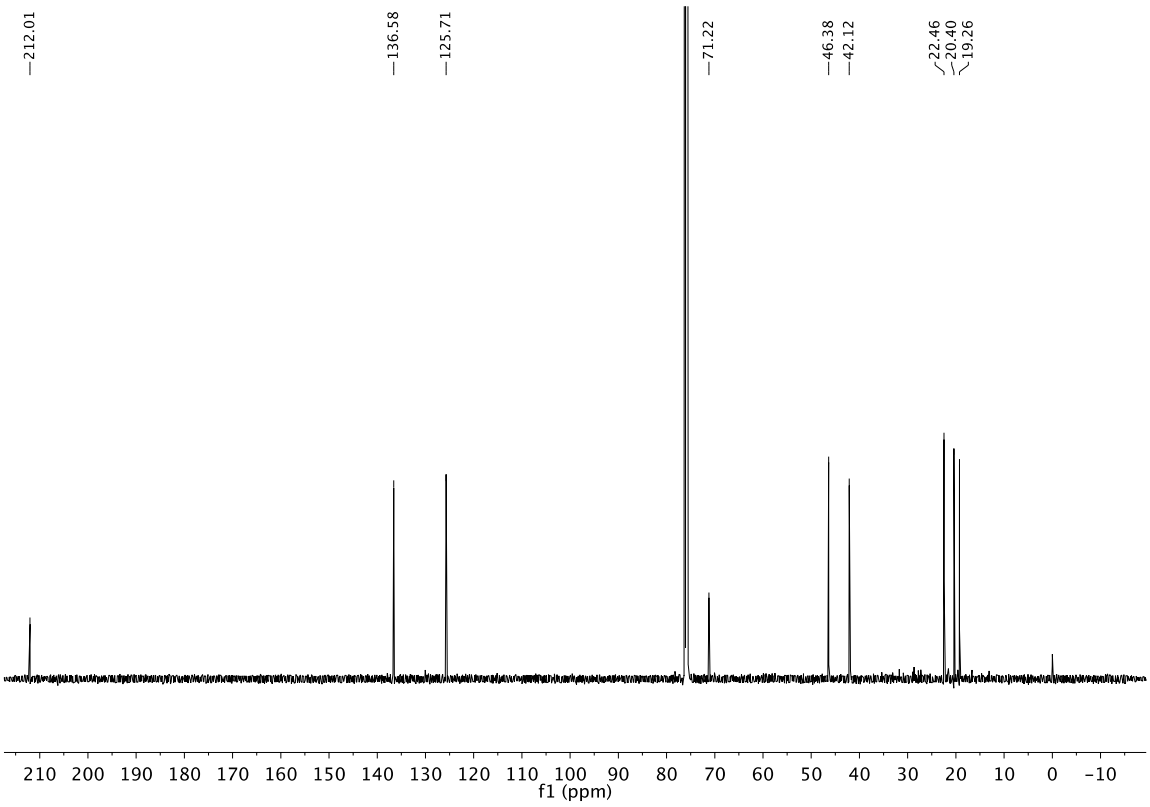
^{1}H NMR: (500 MHz, $CDCl_3$): δ 6.59 - 6.48 (m, 1H), 6.18 (ddd, *J* = 8.1, 6.5, 1.7 Hz, 1H), 3.22 (ddt, *J* = 6.7, 3.3, 1.5 Hz, 1H), 2.94 - 2.80 (m, 1H), 2.33 (s, 1H), 1.92 (ddt, *J* = 12.8, 9.7, 3.1 Hz, 1H), 1.88 - 1.80 (m, 1H), 1.63 (ddd, *J* = 13.1, 10.9, 3.3 Hz, 1H), 1.47 (tdd, *J* = 12.3, 5.5, 2.7 Hz, 1H), 1.32 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$): δ = 212.0, 136.6, 125.7, 71.2, 46.4, 42.1, 22.5, 20.4, 19.3 ppm.

HRMS: (ESI) Calculated for $C_9H_{12}O_2Na$ [M+Na^+] = 175.0730, Found 175.0728.

FTIR: (neat): 2929, 2363, 2341, 1738, 1365 cm^{-1}.

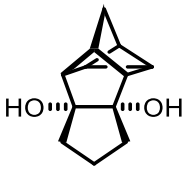

0.83
0.85
0.82
0.87
1.01
0.95
0.93
1.06
1.25
2.91
f1 (ppm)


212.01
136.58
125.71
71.22
46.38
42.12
22.46
20.40
19.26
f1 (ppm)

General Procedure and Spectral Data for Cycloaddition Reactions with Norbornadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), diol (0.30 mmol, 100 mol%) and norbornadiene (0.15 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **5.4a**-**5.4e** and **5.4g**.

(3b*RS*,6a*SR*)-octahydro-3b*H*-2,3,7-(epimethanetriyl)cyclopenta[*a*]pentalene-3b,6a(4*H*)-diol (5.4a)



The reaction was conducted with *cis*-cyclopentane-1,2-diol **5.2a** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 25:75) provided the title compound **5.4a** (46.2 mg, 0.24 mmol) in 80% yield as a white solid.

TLC (SiO_2): R_f = 0.25 (AcOEt:hexanes = 3:7).

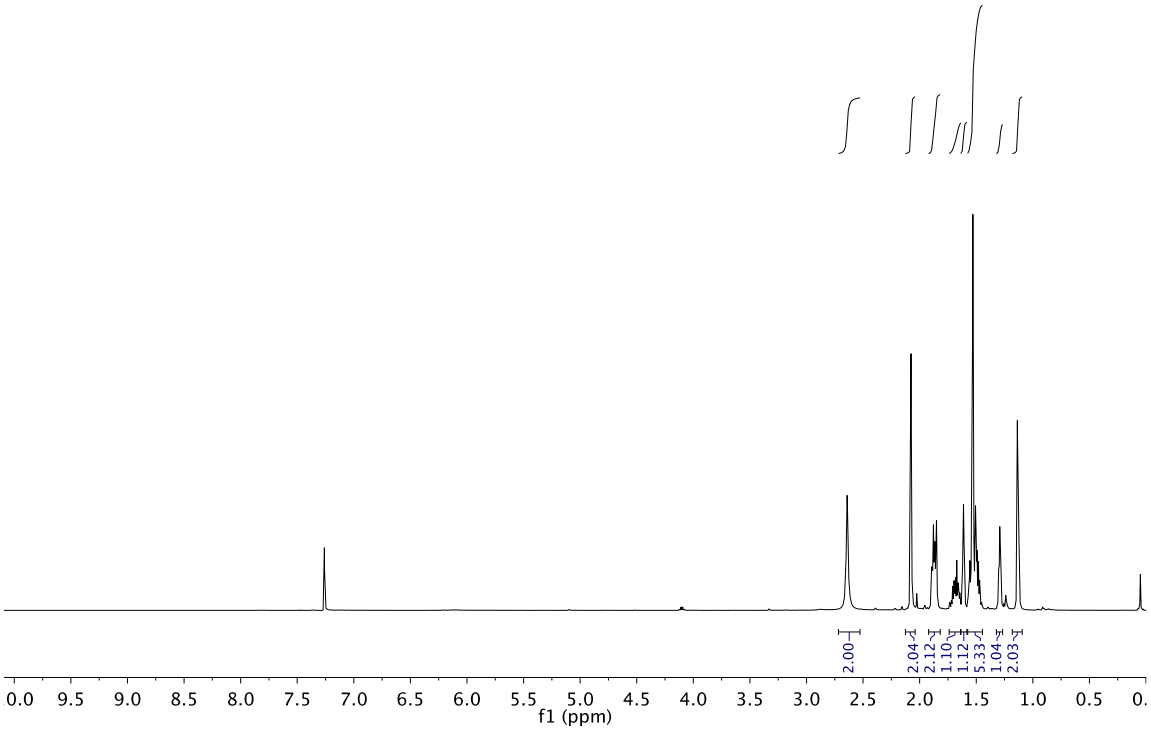
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 2.59 (s, 2H), 2.03 (d, *J* = 2.1 Hz, 2H), 1.87 - 1.77 (m, 2H), 1.69 - 1.59 (m, 1H), 1.56 (s, 1H), 1.53 - 1.40 (m, 5H), 1.24 (t, *J* = 5.1 Hz, 1H), 1.08 (d, *J* = 4.8 Hz, 2H) ppm.

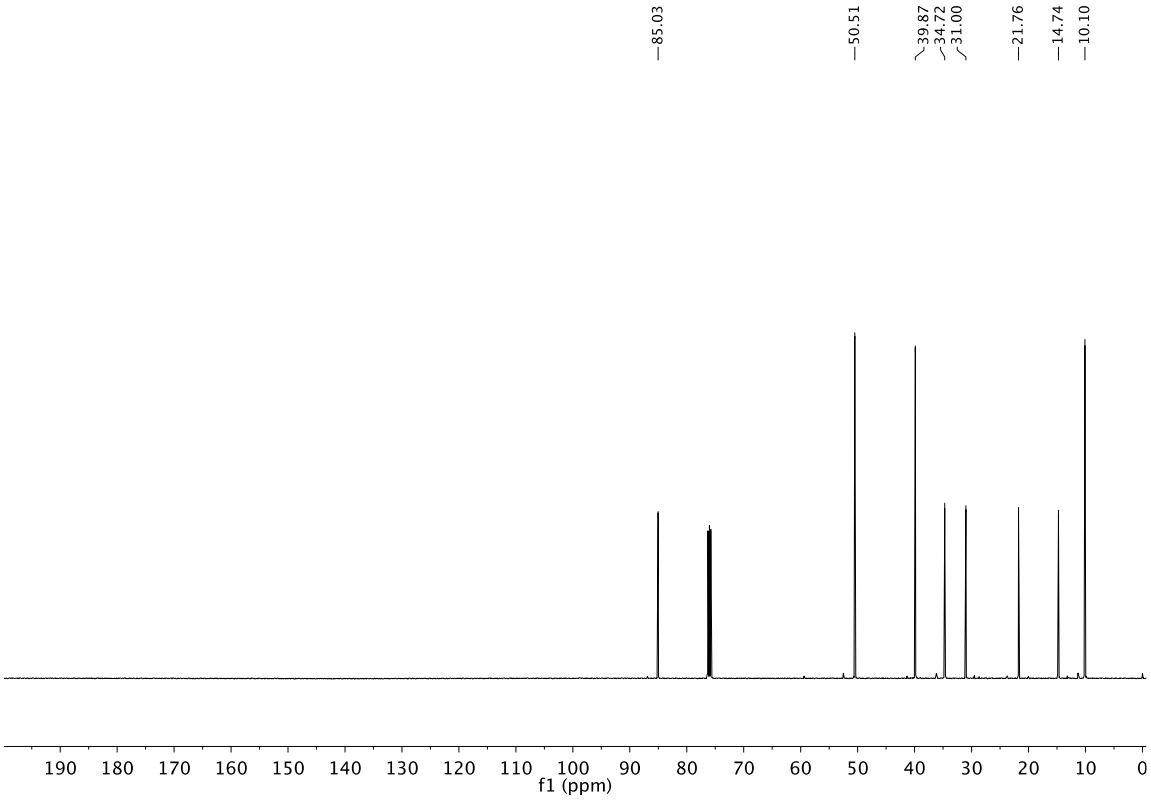
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 85.0, 50.5, 39.9, 34.7, 31.0, 21.8, 14.7, 10.1 ppm.

MP: 59.5-62.0 °C.

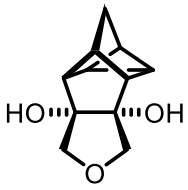
HRMS: (ESI) Calculated for $C_{12}H_{16}O_2Na$ [M+Na^+] =215.1046, Found 215.1043.

FTIR: (neat): 3214, 2922, 2364, 1739 cm^{-1}.


2.00
2.04
2.12
1.10
1.12
5.33
1.04
2.03
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


85.03
50.51
39.87
34.72
31.00
21.76
14.74
10.10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(3a*RS*,7a*SR*)-hexahydro-4,5,7-(epimethanetriyl)pentaleno[1,2-*c*]furan-3a,7a(1*H*,3*H*)-diol (5.4b)



The reaction was conducted with cis-3,4-tetrahydrofuran-diol **5.2b** in accordance with the general procedure using dppb (1,4-bis(diphenylphosphino)butane) at 150 ˚C for 72 h. Flash column chromatography (SiO_2, AcOEt:hexanes = 60:40) provided the title compound **5.4b** (36.7 mg, 0.19 mmol) in 63% yield as a slightly yellow solid.

TLC (SiO_2): R_f = 0.44 (AcOEt : hexanes = 2:1).

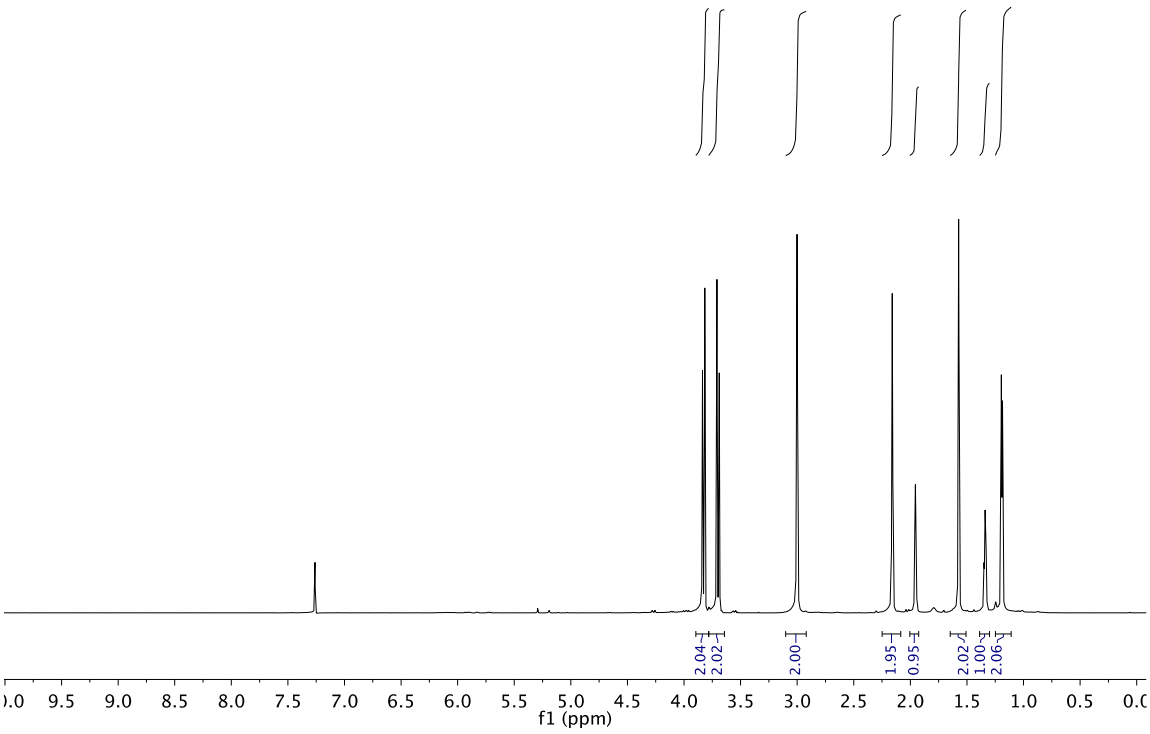
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 3.83 (d, *J* = 10.1 Hz, 2H), 3.70 (d, *J* = 10.2 Hz, 2H), 3.00 (s, 2H), 2.25 - 2.08 (m, 2H), 1.95 (s, 1H), 1.57 (t, *J* = 1.5 Hz, 2H), 1.34 (dt, *J* = 4.9, 2.6 Hz, 1H), 1.19 (d, *J* = 4.9 Hz, 2H) ppm.

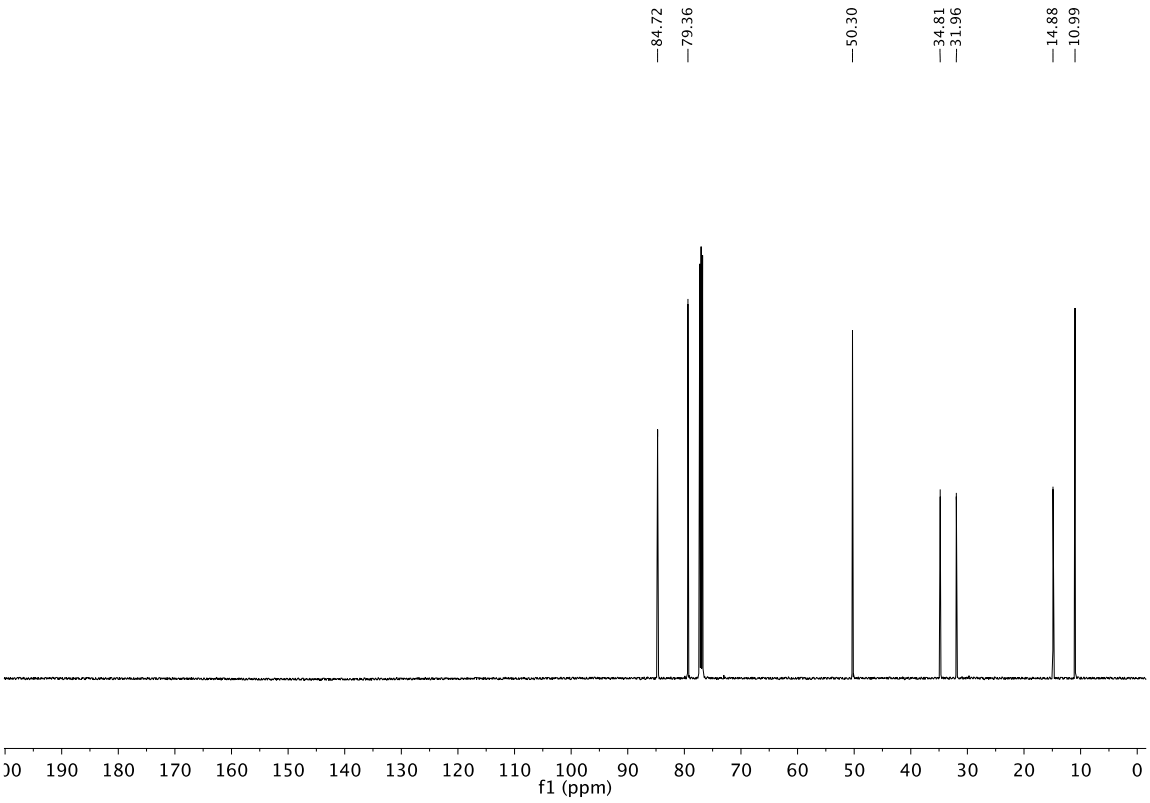
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 84.7, 79.4, 50.3, 34.8, 32.0, 14.9, 11.0 ppm.

MP: 148.6 - 149.5 °C.

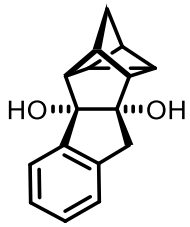
HRMS: (ESI) Calculated for $C_{11}H_{14}O_3Na$ [M+Na^+] = 217.0835, Found 217.0838.

FTIR: (neat): 3383, 2935, 2872 cm^{-1}.


2.04
2.02
2.00
1.95
0.95
2.02
1.00
2.06
f1 (ppm)


84.72
79.36
50.30
34.81
31.96
14.88
10.99
f1 (ppm)

(3b*SR*,8a*SR*)-1,2,3,3a,9,9a-hexahydro-3b*H*-2,3,9-(epimethanetriyl)pentaleno[1,2-*a*]indene-3b,8a(8*H*)-diol (5.4c)



The reaction was conducted with mixture of 1,2- *trans*- and *cis*- dihydroindene diol **5.2c** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 20:80) provided the title compound **5.4c** (59.1 mg, 0.25 mmol) in 82% yield as a white solid.

TLC (SiO_2): R_f = 0.30 (AcOEt:hexanes = 3:7).

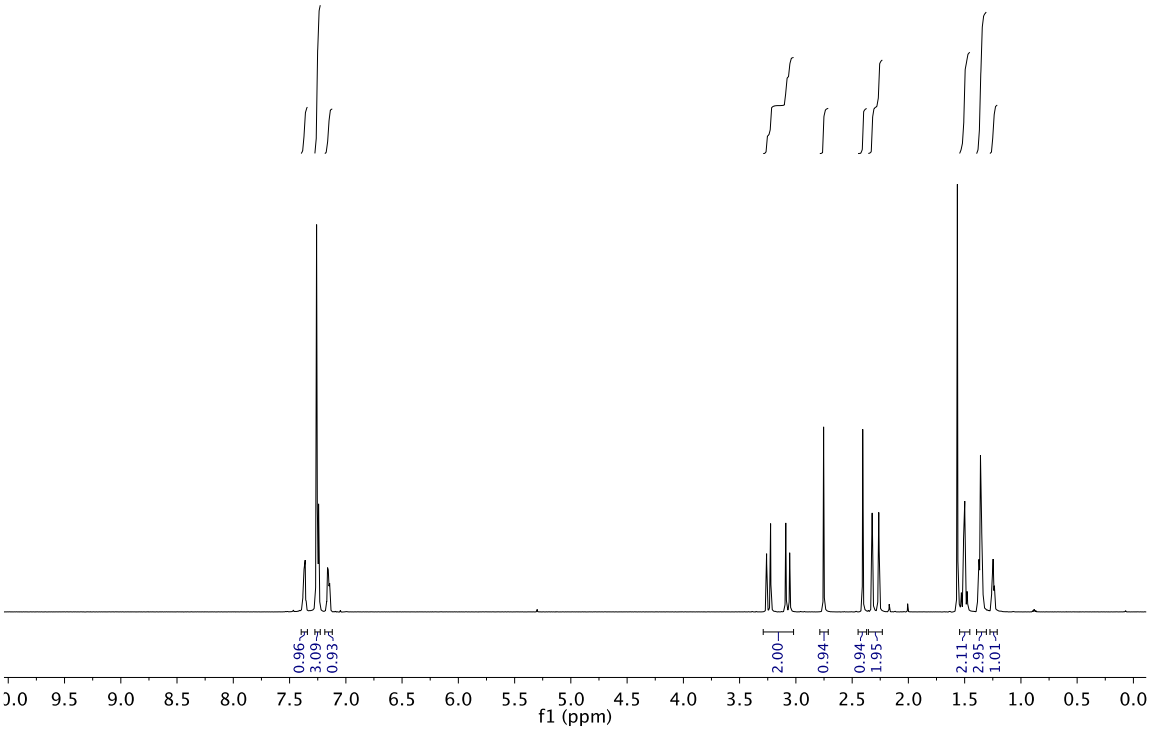
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 5.4, 3.4 Hz, 1H), 7.28 - 7.23 (m, 2H), 7.19 - 7.12 (m, 1H), 3.29 - 3.02 (m, 2H), 2.75 (s, 1H), 2.41 (s, 1H), 2.29 (dt, *J* = 28.9, 2.0 Hz, 2H), 1.54 - 1.45 (m, 2H), 1.39 - 1.31 (m, 3H), 1.25 (td, *J* = 5.7, 1.7 Hz, 1H) ppm.

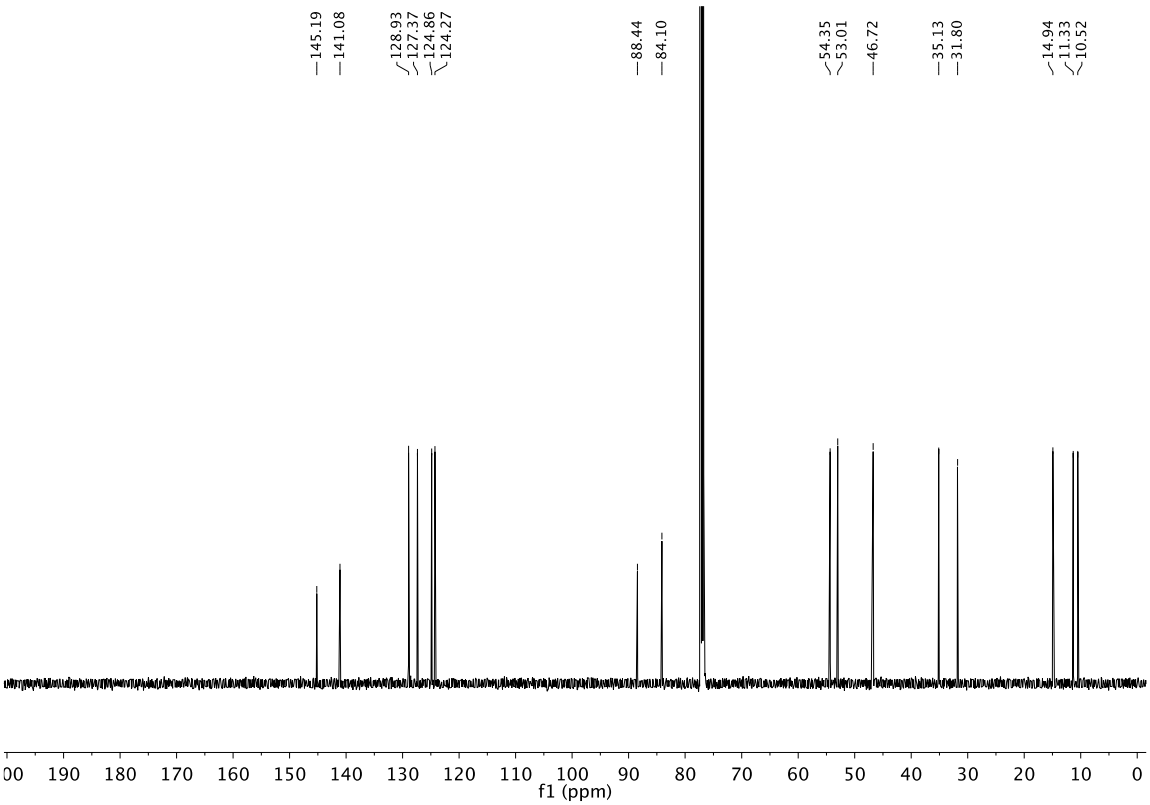
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 145.2, 141.1, 128.9, 127.4, 124.9, 124.3, 88.4, 84.1, 54.4, 53.0, 46.7, 35.1, 31.8, 14.9, 11.3, 10.5 ppm.

MP: 115.8-119.4 °C.

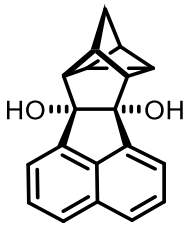
HRMS: (ESI) Calculated for $C_{16}H_{16}O_2Na$ [M+Na^+] = 263.1043, Found 263.1043.

FTIR: (neat): 3399, 2940, 2365, 1743 cm^{-1}.


0.96
3.09
0.93
2.00
0.94
0.94
1.95
2.11
2.95
1.01
f1 (ppm)


145.19
141.08
128.93
127.37
124.86
124.27
88.44
84.10
54.35
53.01
46.72
35.13
31.80
14.94
11.33
10.52
f1 (ppm)

(6b*RS*,10a*SR*)-6c,7,8,9,9a,10-hexahydro-7,8,10-(epimethanetriyl)pentaleno[1,2-*a*]acenaphthylene-6b,10a-diol (5.4d)



The reaction was conducted with mixture of *trans*- and *cis*- acenaphthylene diol **5.2d** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 15:85) provided the title compound **5.4d** (75.4 mg, 0.27 mmol) in 91% yield as a white solid.

TLC (SiO_2): R_f = 0.30 (AcOEt:hexanes = 3:7).

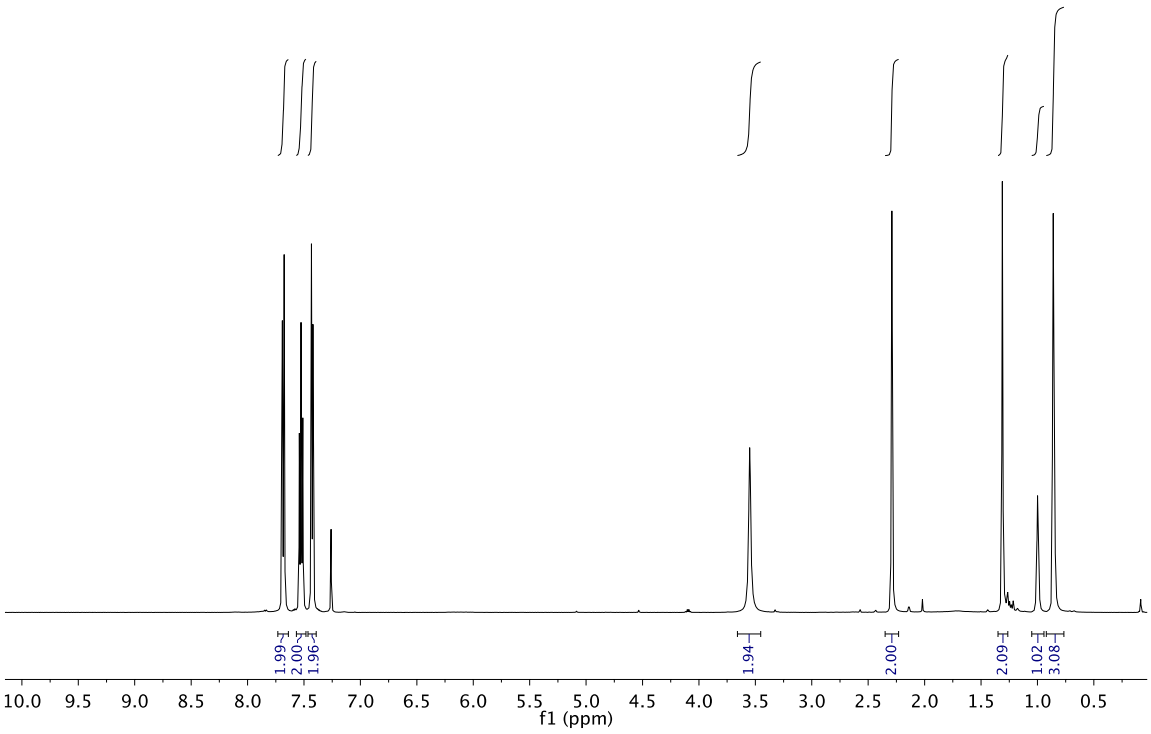
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 2H), 3.55 (s, 2H), 2.29 (s, 2H), 1.31 (s, 2H), 0.99 (d, *J* = 5.0 Hz, 1H), 0.85 (d, *J* = 5.3 Hz, 3H). ppm.

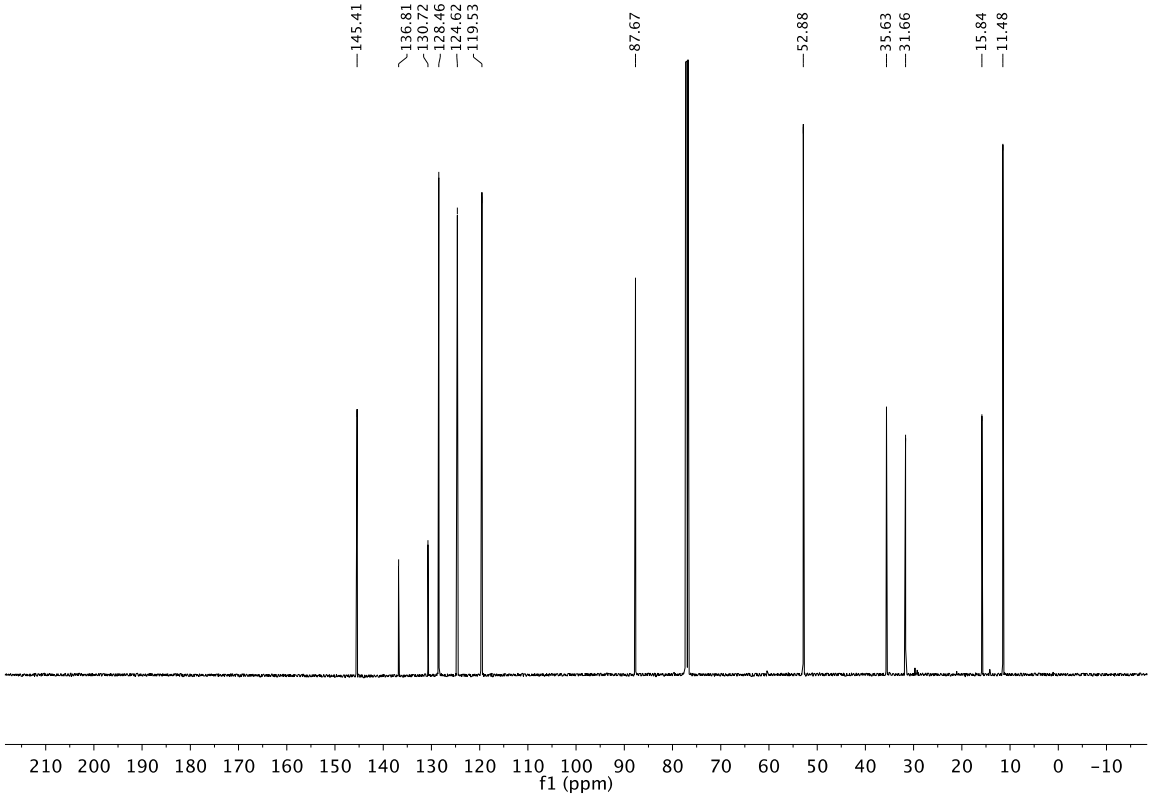
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 145.4, 136.8, 130.7, 128.5, 124.6, 119.5, 87.7, 52.9, 35.6, 31.7, 15.8, 11.5 ppm.

MP: 188.2-190.5°C.

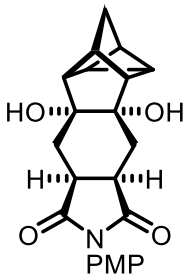
HRMS: (ESI) Calculated for $C_{19}H_{16}O_2Na$ [M+Na^+] =299.1043, Found 299.1042.

FTIR: (neat): 3437, 2942, 2364, 1739 cm^{-1}.


1.99
2.00
1.96
1.94
2.00
2.09
1.02
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


145.41
136.81
130.72
128.46
124.62
119.53
87.67
52.88
35.63
31.66
15.84
11.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(3a*RS*,4a*SR*,8a*RS*,9a*SR*)-4a,8a-dihydroxy-2-(4-methoxyphenyl)dodecahydro-1*H*-5,6,8-(epimethanetriyl)pentaleno[1,2-*f*]isoindole-1,3(2*H*)-dione (5.4e)



The reaction was conducted with (3a*RS*,5*RS*,6*SR*,7a*SR*)-5,6-phthalimide diol **5.2e** in accordance with the general procedure. Flash column chromatography (SiO_2, EtOAc:hexane = 75:25) provided the title compound **5.4e** (65.0 mg, 0.26 mmol) in 85% yield as a white solid.

TLC (SiO_2): R_f = 0.52 (AcOEt:hexanes = 4:1).

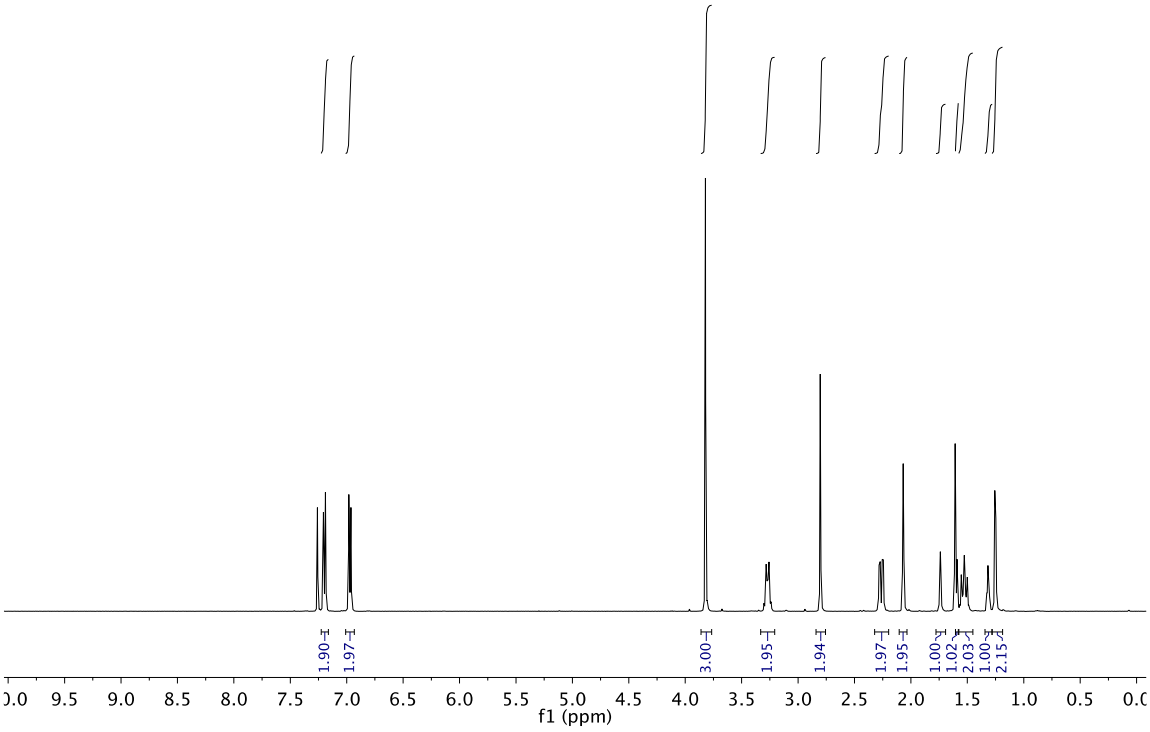
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.23 - 7.16 (m, 2H), 7.01 - 6.93 (m, 2H), 3.82 (s, 3H), 3.33 - 3.21 (m, 2H), 2.80 (s, 2H), 2.26 (dd, *J* = 14.4, 4.9 Hz, 2H), 2.10 - 2.03 (m, 2H), 1.74 (s, 1H), 1.60 (d, *J* = 8.7 Hz, 2H), 1.58 - 1.45 (m, 2H), 1.32 (t, *J* = 5.0 Hz, 1H), 1.25 (d, *J* = 4.8 Hz, 2H) ppm.

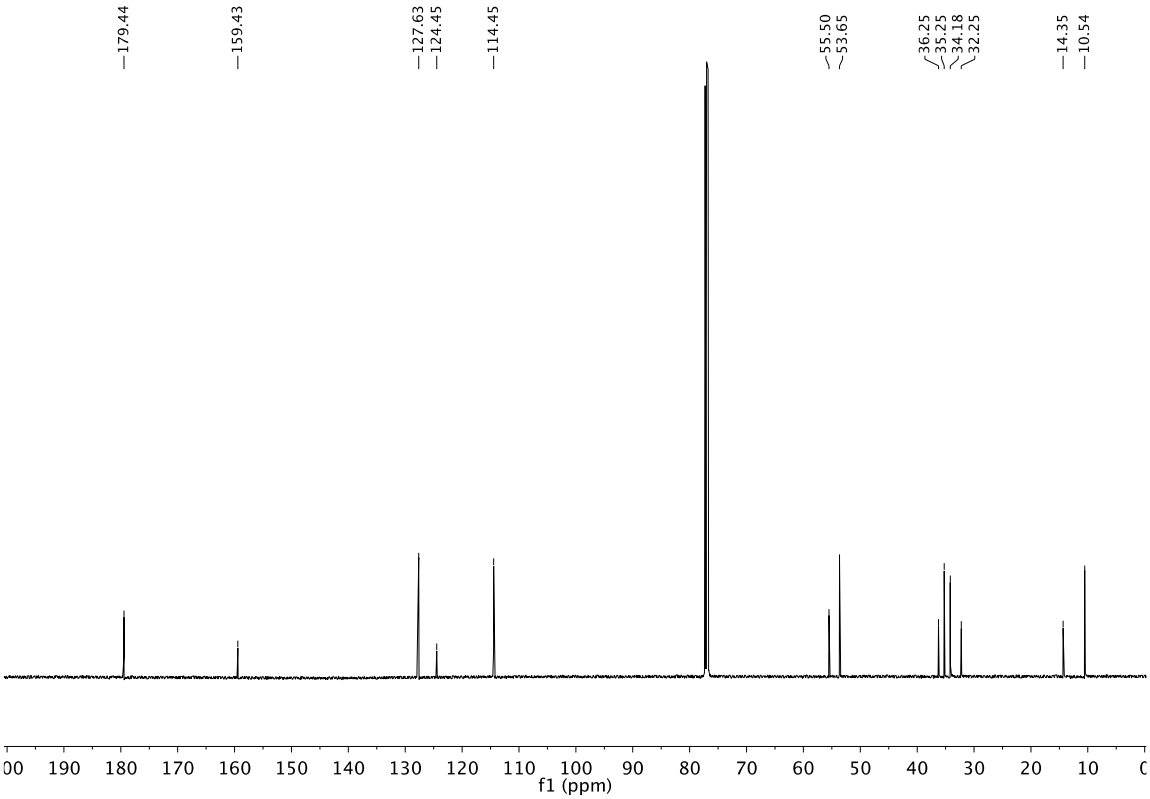
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 179.4, 159.4, 127.6, 124.5, 114.5, 55.5, 53.7, 36.3, 35.3, 34.2, 32.3, 14.4, 10.5 ppm.

MP: 228.3 - 230.4 °C.

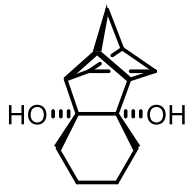
HRMS: (ESI) Calculated for $C_{22}H_{24}NO_5$ [M+H$^+$] = 382.1649, Found 382.1652.

FTIR: (neat): 3387, 2921, 1687 cm^{-1}.


1.90
1.97
3.00
1.95
1.94
1.97
1.95
1.00
1.02
2.03
1.00
2.15
f1 (ppm)


179.44
159.43
127.63
124.45
114.45
55.50
53.65
36.25
35.25
34.18
32.25
14.35
10.54
f1 (ppm)

(3b*SR*,8a*SR*)-1,2,3,3a,9,9a-hexahydro-3b*H*-2,3,9-(epimethanetriyl)pentaleno[1,2-*a*]indene-3b,8a(8*H*)-diol (5.4g)



The reaction was conducted with *trans*-1,2-hexane diol **5.2g** in accordance with the general procedure. Flash column chromatography (SiO_2, AcOEt:hexanes = 25:75) provided the title compound **5.4g** (33.4 mg, 0.16 mmol) in 54% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (AcOEt:hexanes = 3:7).

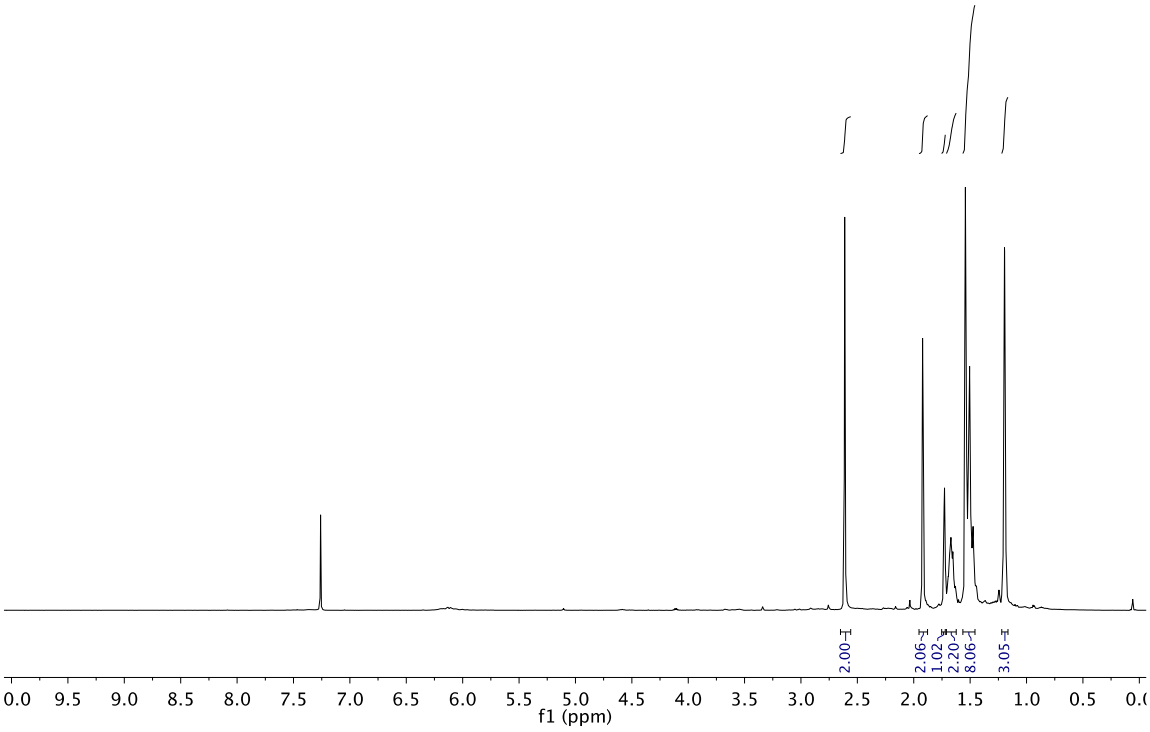
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 2.61 (s, 2H), 1.92 (d, *J* = 2.1 Hz, 2H), 1.73 (s, 1H), 1.66 (tdd, *J* = 12.4, 6.3, 2.1 Hz, 2H), 1.56 - 1.46 (m, 8H), 1.20 (s, 3H) ppm.

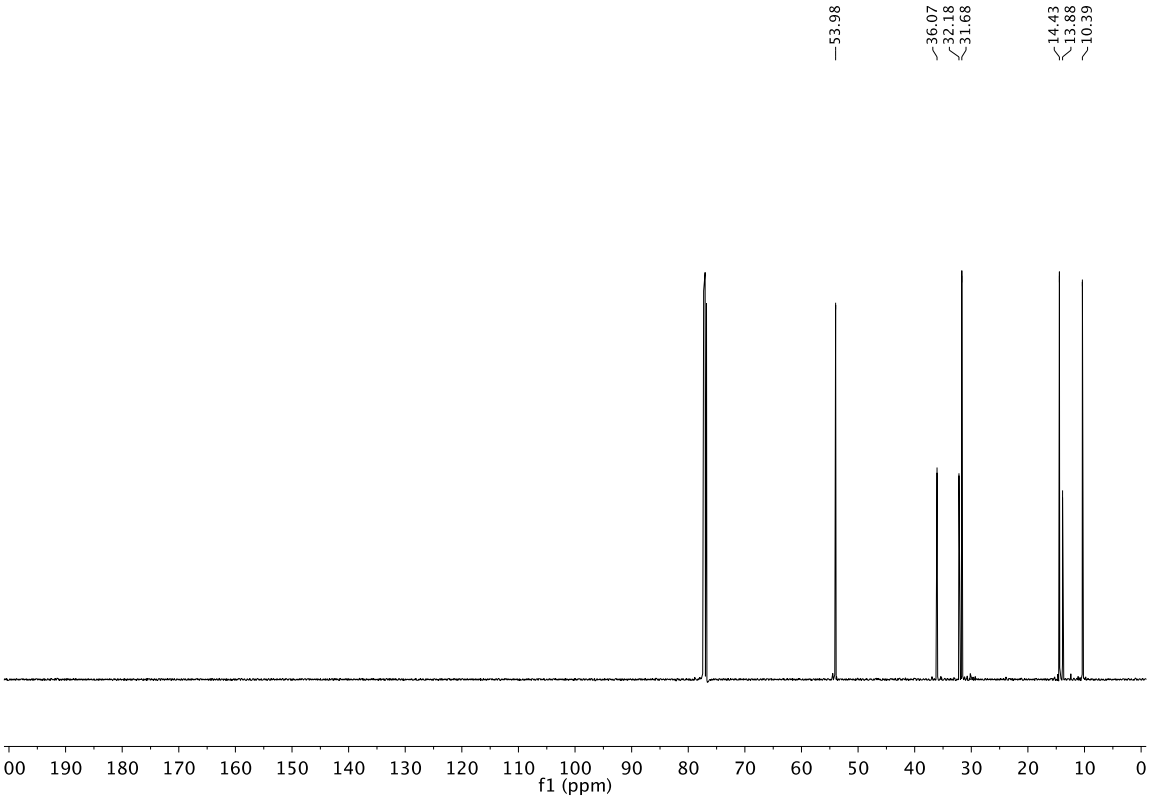
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 54.0, 36.1, 32.2, 31.7, 14.4, 13.9, 10.4 ppm.

MP: 114.2-116.5 °C.

HRMS: (ESI) Calculated for $C_{13}H_{18}O_6Na$ [M+Na^+] =229.1199, Found 229.1197.

FTIR: (neat): 3279, 2927, 2364, 1205 cm^{-1}.


2.00
2.06
1.02
2.20
8.06
3.05
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


53.98
36.07
32.18
31.68
14.43
13.88
10.39
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

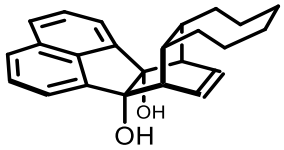
Procedure for Cycloaddition Reactions with Non-Conjugated Alkenes

Reaction with 1,4-Cycohexadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), 3,5-Me_2BzOH (4.5 mg, 0.03 mmol, 10 mol%), *cis*-1,2 cyclopentane diol **5.2a** (30.6 mg, 0.3 mmol, 100 mol%) and 1,4-cyclohexadiene (0.14 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 140 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, AcOEt:hexanes = 25:75), which provided the title compound **5.3a** (51.2 mg, 0.29 mmol) in 95% yield as a white solid. The characterization data of the furnished compound matched with that provided from 1,3-cyclohexadiene in all respects.

Reaction with 1,5,9-Cyclododecatriene

(6bRS,7RS,7aRS,13aSR,14SR,14aRS)-7,7a,8,9,10,11,12,13,13a,14-decahydro-7,14-ethenocycloocta[k]fluoranthene-6b,14a-diol (5.3d')



A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), mixture of *trans*- and *cis*- acenaphthylene diol **5.2d** (55.9 mg, 0.3 mmol, 100 mol%) and 1,5,9-cyclododecatriene (0.27 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, AcOEt:hexanes = 13:87), which provided the title compound **5.3d'** (44.6 mg, 0.13 mmol) in 43% yield as a white solid.

TLC (SiO_2): R_f = 0.32 (AcOEt:hexanes = 3:7).

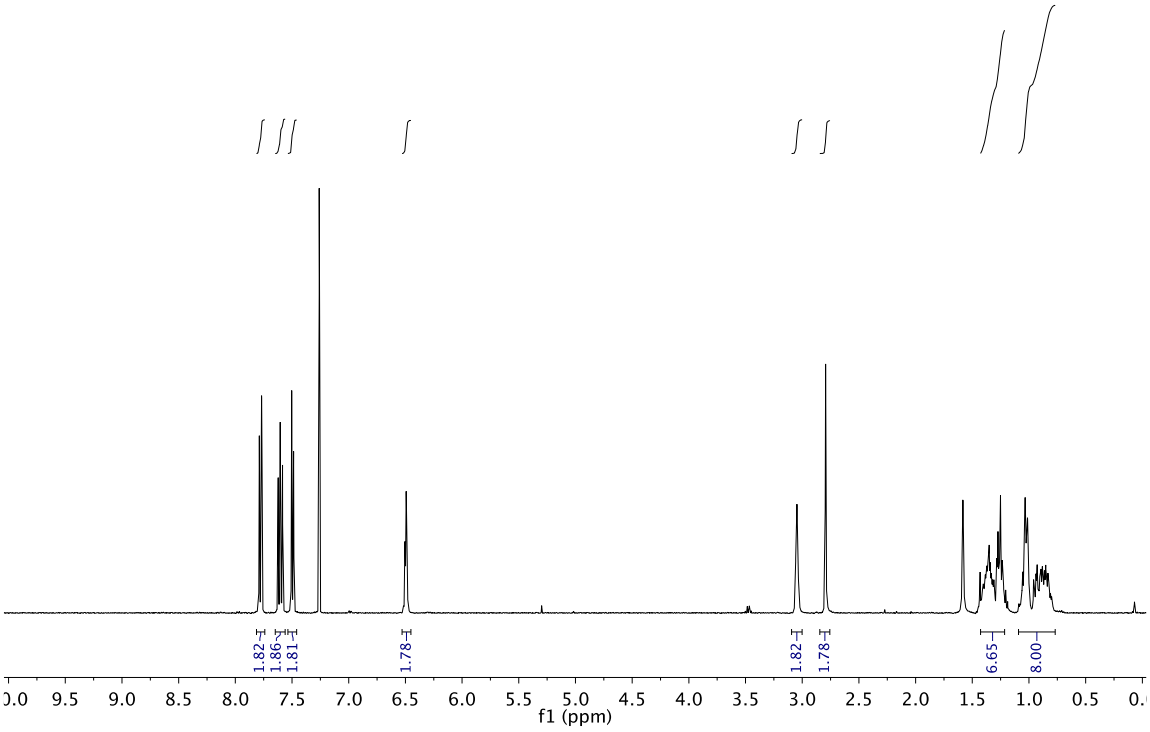
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.78 (dd, *J* = 8.3, 0.7 Hz, 2H), 7.60 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.50 (dd, *J* = 7.0, 0.8 Hz, 2H), 6.53 - 6.45 (m, 2H), 3.09 - 3.00 (m, 2H), 2.79 (d, *J* = 1.0 Hz, 2H), 1.43 - 1.22 (m, 6H), 1.03 (td, *J* = 8.3, 5.9 Hz, 4H), 0.98 - 0.77 (m, 4H) ppm.

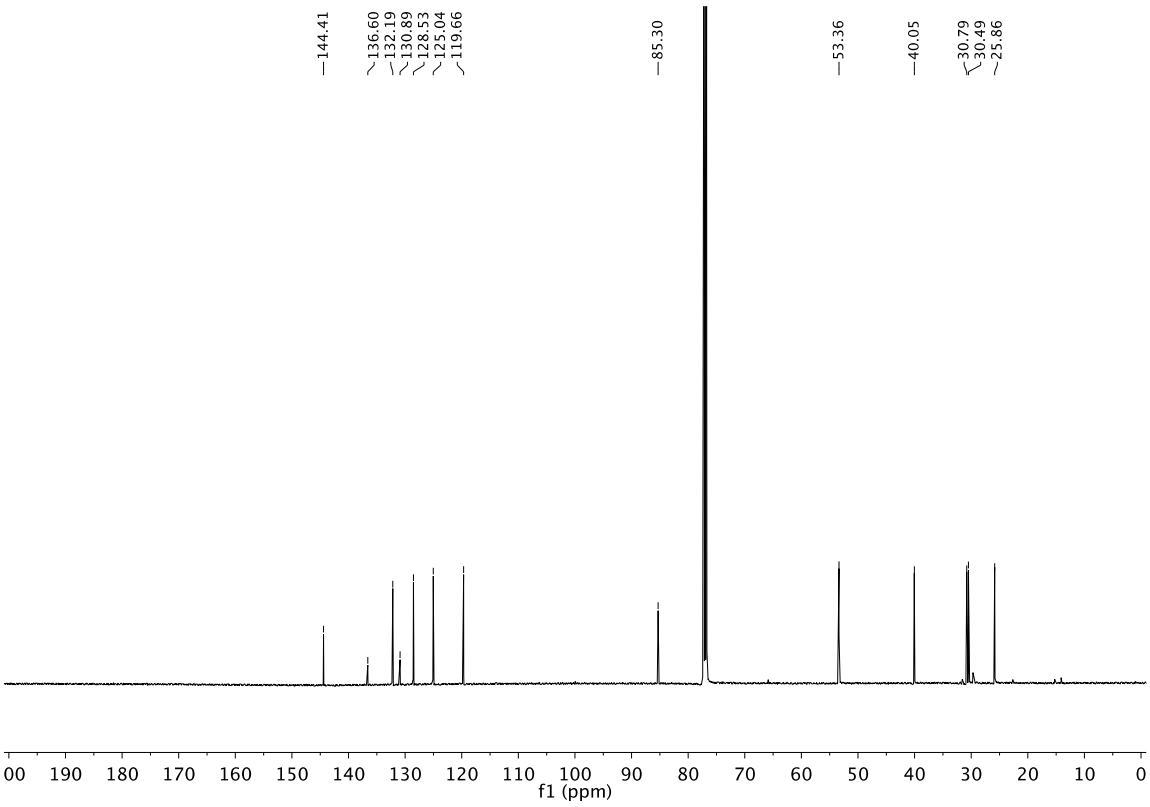
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 144.4, 136.2, 132.2, 130.9, 128.5, 125.1, 119.7, 85.3, 53.4, 40.1, 30.8, 30.5, 25.9 ppm.

MP: 136 - 138 °C.

HRMS: (ESI) Calculated for $C_{24}H_{26}O_2Na$ $[M+Na^+]$ =369.1825, Found 369.1832.

FTIR: (neat): 3363, 3047, 2921, 2851, 1494, 1363 cm^{-1}.


1.82
1.86
1.81
1.78
1.82
1.78
6.65
8.00
f1 (ppm)


144.41
136.60
132.19
130.89
128.53
125.04
119.66
85.30
53.36
40.05
30.79
30.49
25.86
f1 (ppm)

Procedure for Redox Level Independent Cycloaddition Reactions.

Reaction of *Dehydro*-5.*2g with* Norbornadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (3.8 mg, 0.006 mmol, 2 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), ketol dimer (34.2 mg, 0.15 mmol, 100 mol%) and norbornadiene (0.15 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, AcOEt:hexanes = 20:80), which provided the title compound **5.4g** (38.4 mg, 0.186 mmol) in 62% yield as a white solid. The characterization data of the furnished compound matched with that provided from **5.2g** in all respects.

Reaction *with* 1,3-Cyclohexadiene

From *dehydro*-**5.2d**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (2.6 mg, 0.004 mmol, 2 mol%), dppe (4.8 mg, 0.012 mmol, 6 mol%), 3,5-Me_2BzOH (3.0 mg, 0.02 mmol, 10 mol%), *dehydro*-**5.2d** (36.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.1 mL, 2.0 M) and **5.1a** (99 μL, 1.0 mmol, 500 mol%) were added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 140 ˚C for 40 hours. After cooling to room temperature, the mixture was purified by flash column chromatography (SiO_2: AcOEt:hexanes= 25:75) to give **5.3d** (50.8 mg, 0.19 mmol) in 95% yield as a slightly yellow solid.

From *didehydro*-**5.2d**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (2.6 mg, 0.004 mmol, 2 mol%), dppe (4.8 mg, 0.012 mmol, 6 mol%), 3,5-Me_2BzOH (3.0 mg, 0.02 mmol, 10 mol%), *didehydro*-**5.2d** (36.4 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.1 mL, 2.0 M), **5.1a** (99 μL, 1.0 mmol, 500 mol%) and formic acid (17 μL, 88% in H_2O, 0.4 mmol, 200 mol%) were added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 140 ˚C for 40 hours. After cooling to room temperature, the mixture was purified by flash column chromatography (SiO_2: AcOEt:hexanes = 25:75) to give **5.3d** (34.4 mg, 0.13 mmol) in 64% yield as a slightly yellow solid.

Reaction *with* Norbornadiene

From *dehydro*-**5.2d**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (2.6 mg, 0.004 mmol, 2 mol%), dppe (4.8 mg, 0.012 mmol, 6 mol%) and *dehydro*-**5.2d** (36.8 mg, 0.2 mmol, 100 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.1 mL, 2.0 M) and **5.1c** (102 μL, 1.0 mmol, 500 mol%) were added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was purified by flash column chromatography (SiO_2: AcOEt:hexanes = 25:75) to give **5.4d** (37.4 mg, 0.14 mmol) in 68% yield as a slightly yellow solid.

From *didehydro*-**5.2d**:

A resealable pressure tube (ca. 13 x 100 mm) was charged with [$Ru_3(CO)_{12}$] (2.6 mg, 0.004 mmol, 2 mol%), dppe (4.8 mg, 0.012 mmol, 6 mol%) and *didehydro*-**5.2d** (36.4 mg, 0.2 mmol, 100

mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.1 mL, 2.0 M), **5.1c** (102 μL, 1.0 mmol, 500 mol%) and formic acid (17 μL, 88% in H_2O, 0.4 mmol, 200 mol%) were added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was purified by flash column chromatography (SiO_2: AcOEt:hexanes = 75:25) to give **5.4d** (40.5 mg, 0.15 mmol) in 73% yield as a slightly yellow solid.

Procedure for Cycloaddition Reactions with Dihydride Complex $H_2Ru(CO)(PPh_3)_3$

Reaction of 5.2a *with* 1,3-Cyclohexadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with $H_2Ru(CO)(PPh_3)_3$ (16.5 mg, 0.018 mmol, 6 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), 3,5-Me_2BzOH (4.5 mg, 0.03 mmol, 10 mol%), *cis*-cyclopentane-1,2-diol (30.6 mg, 0.3 mmol, 100 mol%) and 1,3-cyclohexadiene (0.15 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 140 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, AcOEt:hexanes = 25:75) provided **5.3a** (50.3 mg, 0.19 mmol) in 93% yield as a white solid.

Reaction of 5.2a *with* Norbornadiene

A resealable pressure tube (ca. 13 x 100 mm) was charged with $H_2Ru(CO)(PPh_3)_3$ (16.5 mg, 0.018 mmol, 6 mol%), dppe (7.2 mg, 0.018 mmol, 6 mol%), *cis*-cyclopentane-1,2-diol (30.6 mg, 0.3 mmol, 100 mol%) and norbornadiene (0.15 mL, 1.5 mmol, 500 mol%). The reaction vessel was placed under an atmosphere of argon, and PhMe (0.15 mL, 2.0 M) was added. The reaction vessel was sealed and the reaction mixture was allowed to stir at 130 ˚C for 40 hours. After cooling to room temperature, the mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, AcOEt:hexanes = 25:75) provided **5.4a** (38.4 mg, 0.13 mmol) in 67% yield as a white solid.

Single Crystal Diffraction Data

X-ray Experimental for complex **5.3b**-CH_2Cl_2

X-ray Experimental for complex $C_{10}H_{14}O_3$: Crystals grew as thin, colorless needles by slow evaporation fromCH_2Cl_2/pentane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.25 x 0.06 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 1058 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 12 seconds per frame with a detector offset of +/- 41.6° and 32 seconds per frame with a detector offset of +/- 109.0°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.[29] The structure was solved by direct methods using SHELXT[30] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON[31] and WinGX.[32] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma w(|Fo|2 - |Fc|2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.1*P)^2]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.151, with R(F) equal to 0.0445 and a goodness of fit, S, = 1.07. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[33] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[34] All figures were generated using

SHELXTL/PC.[35] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.3. Crystal data and structure refinement for **5.3b**.

Empirical formula	C10 H14 O3	
Formula weight	182.21	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.1033(9) Å	α= 90°.
	b = 6.2090(3) Å	β= 110.335(5)°.
	c = 14.4437(8) Å	γ = 90°.
Volume	1690.52(15) $Å^3$	
Z	8	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	0.861 mm^{-1}	
F(000)	784	
Crystal size	0.260 x 0.060 x 0.020 mm^3	
Theta range for data collection	3.263 to 75.732°.	
Index ranges	-24<=h<=21, -7<=k<=7, -18<=l<=17	
Reflections collected	10619	
Independent reflections	3446 [R(int) = 0.0314]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.899	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3446 / 0 / 240	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1852	
R indices (all data)	R1 = 0.0773, wR2 = 0.1924	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.951 and -0.327 $e.Å^{-3}$	

Table 5.4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.3b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	8825(1)	1928(4)	4450(2)	19(1)
C2	8834(1)	3958(4)	5056(2)	16(1)
C3	9385(1)	3393(4)	6112(2)	15(1)
C4	9598(1)	1074(4)	5985(2)	18(1)
C5	8114(1)	4522(4)	5155(2)	17(1)
C6	8246(1)	6343(4)	5891(2)	18(1)
C7	8716(1)	5895(4)	6782(2)	18(1)
C8	9008(1)	3632(4)	6873(2)	16(1)
C9	8375(1)	2081(4)	6630(2)	18(1)
C10	7837(1)	2588(4)	5586(2)	16(1)
C11	6129(1)	8212(4)	543(2)	19(1)
C12	6147(1)	6195(4)	1157(2)	16(1)
C13	5618(1)	6745(4)	1718(2)	16(1)
C14	5383(1)	9051(4)	1376(2)	19(1)
C15	6886(1)	5694(4)	1932(2)	17(1)
C16	7164(1)	7653(4)	2615(2)	17(1)
C17	6648(1)	8149(4)	3173(2)	18(1)
C18	6022(1)	6544(4)	2840(2)	16(1)
C19	6328(1)	4299(4)	3024(2)	18(1)
C20	6783(1)	3871(4)	2561(2)	18(1)
O1	9044(1)	198(3)	5147(1)	18(1)
O2	9067(1)	5685(3)	4591(1)	18(1)
O3	9978(1)	4783(3)	6432(1)	19(1)
O4	5921(1)	9944(3)	1038(1)	18(1)
O5	5912(1)	4447(3)	484(1)	18(1)
O6	5035(1)	5322(3)	1498(1)	19(1)

—

Table 5.5. Bond lengths [Å] and angles [°] for **5.3b**.

C1-O1	1.432(3)	C11-H11A	0.99
C1-C2	1.531(3)	C11-H11B	0.99
C1-H1A	0.99	C12-O5	1.424(3)
C1-H1B	0.99	C12-C15	1.549(3)
C2-O2	1.428(3)	C12-C13	1.584(3)
C2-C5	1.544(3)	C13-O6	1.412(3)
C2-C3	1.582(3)	C13-C14	1.535(3)
C3-O3	1.412(3)	C13-C18	1.544(3)
C3-C4	1.531(3)	C14-O4	1.443(3)
C3-C8	1.543(3)	C14-H14A	0.99
C4-O1	1.437(3)	C14-H14B	0.99
C4-H4A	0.99	C15-C20	1.510(3)
C4-H4B	0.99	C15-C16	1.544(3)
C5-C6	1.511(4)	C15-H15	1.00
C5-C10	1.542(3)	C16-C17	1.551(3)
C5-H5	1.00	C16-H16A	0.99
C6-C7	1.335(4)	C16-H16B	0.99
C6-H6	0.95	C17-C18	1.544(3)
C7-C8	1.511(3)	C17-H17A	0.99
C7-H7	0.95	C17-H17B	0.99
C8-C9	1.537(3)	C18-C19	1.509(3)
C8-H8	1.00	C18-H18	1.00
C9-C10	1.552(3)	C19-C20	1.334(4)
C9-H9A	0.99	C19-H19	0.95
C9-H9B	0.99	C20-H20	0.95
C10-H10A	0.99	O2-H2	0.84
C10-H10B	0.99	O3-H3	0.84
C11-O4	1.432(3)	O5-H5A	0.84
C11-C12	1.527(3)	O6-H6A	0.84

O1-C1-C2	106.0(2)	C4-C3-C8	113.8(2)
O1-C1-H1A	110.5	O3-C3-C2	114.1(2)
C2-C1-H1A	110.5	C4-C3-C2	102.9(2)
O1-C1-H1B	110.5	C8-C3-C2	108.23(19)
C2-C1-H1B	110.5	O1-C4-C3	106.8(2)
H1A-C1-H1B	108.7	O1-C4-H4A	110.4
O2-C2-C1	106.9(2)	C3-C4-H4A	110.4
O2-C2-C5	110.1(2)	O1-C4-H4B	110.4
C1-C2-C5	114.5(2)	C3-C4-H4B	110.4
O2-C2-C3	112.8(2)	H4A-C4-H4B	108.6
C1-C2-C3	103.54(19)	C6-C5-C10	107.4(2)
C5-C2-C3	109.0(2)	C6-C5-C2	107.1(2)
O3-C3-C4	112.0(2)	C10-C5-C2	110.0(2)
O3-C3-C8	106.00(19)	C6-C5-H5	110.7

C10-C5-H5	110.7	C18-C13-C12	108.49(19)
C2-C5-H5	110.7	O4-C14-C13	106.6(2)
C7-C6-C5	114.5(2)	O4-C14-H14A	110.4
C7-C6-H6	122.8	C13-C14-H14A	110.4
C5-C6-H6	122.8	O4-C14-H14B	110.4
C6-C7-C8	113.6(2)	C13-C14-H14B	110.4
C6-C7-H7	123.2	H14A-C14-H14B	108.6
C8-C7-H7	123.2	C20-C15-C16	107.5(2)
C7-C8-C9	107.2(2)	C20-C15-C12	106.8(2)
C7-C8-C3	107.5(2)	C16-C15-C12	110.3(2)
C9-C8-C3	110.5(2)	C20-C15-H15	110.7
C7-C8-H8	110.5	C16-C15-H15	110.7
C9-C8-H8	110.5	C12-C15-H15	110.7
C3-C8-H8	110.5	C15-C16-C17	109.2(2)
C8-C9-C10	109.7(2)	C15-C16-H16A	109.8
C8-C9-H9A	109.7	C17-C16-H16A	109.8
C10-C9-H9A	109.7	C15-C16-H16B	109.8
C8-C9-H9B	109.7	C17-C16-H16B	109.8
C10-C9-H9B	109.7	H16A-C16-H16B	108.3
H9A-C9-H9B	108.2	C18-C17-C16	109.3(2)
C5-C10-C9	108.8(2)	C18-C17-H17A	109.8
C5-C10-H10A	109.9	C16-C17-H17A	109.8
C9-C10-H10A	109.9	C18-C17-H17B	109.8
C5-C10-H10B	109.9	C16-C17-H17B	109.8
C9-C10-H10B	109.9	H17A-C17-H17B	108.3
H10A-C10-H10B	108.3	C19-C18-C17	107.7(2)
O4-C11-C12	106.2(2)	C19-C18-C13	107.1(2)
O4-C11-H11A	110.5	C17-C18-C13	110.5(2)
C12-C11-H11A	110.5	C19-C18-H18	110.5
O4-C11-H11B	110.5	C17-C18-H18	110.5
C12-C11-H11B	110.5	C13-C18-H18	110.5
H11A-C11-H11B	108.7	C20-C19-C18	113.8(2)
O5-C12-C11	107.1(2)	C20-C19-H19	123.1
O5-C12-C15	110.3(2)	C18-C19-H19	123.1
C11-C12-C15	114.1(2)	C19-C20-C15	114.4(2)
O5-C12-C13	113.0(2)	C19-C20-H20	122.8
C11-C12-C13	103.63(19)	C15-C20-H20	122.8
C15-C12-C13	108.6(2)	C1-O1-C4	105.47(19)
O6-C13-C14	111.9(2)	C2-O2-H2	109.5
O6-C13-C18	106.21(19)	C3-O3-H3	109.5
C14-C13-C18	113.8(2)	C11-O4-C14	105.27(19)
O6-C13-C12	113.7(2)	C12-O5-H5A	109.5
C14-C13-C12	102.8(2)	C13-O6-H6A	109.5

Table 5.6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5.3b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	24(1)	14(1)	19(1)	1(1)	7(1)	1(1)
C2	18(1)	12(1)	17(1)	2(1)	6(1)	2(1)
C3	14(1)	12(1)	19(1)	-1(1)	4(1)	0(1)
C4	17(1)	16(1)	21(1)	1(1)	4(1)	0(1)
C5	14(1)	14(1)	21(1)	2(1)	5(1)	1(1)
C6	18(1)	12(1)	27(1)	1(1)	11(1)	2(1)
C7	21(1)	14(1)	24(1)	-4(1)	12(1)	-3(1)
C8	17(1)	14(1)	17(1)	2(1)	6(1)	-1(1)
C9	18(1)	15(1)	21(1)	2(1)	7(1)	-3(1)
C10	14(1)	12(1)	21(1)	2(1)	4(1)	-2(1)
C11	23(1)	13(1)	21(1)	0(1)	10(1)	2(1)
C12	16(1)	13(1)	18(1)	-1(1)	6(1)	1(1)
C13	17(1)	13(1)	20(1)	2(1)	8(1)	1(1)
C14	21(1)	15(1)	22(1)	0(1)	9(1)	0(1)
C15	17(1)	13(1)	21(1)	0(1)	7(1)	1(1)
C16	14(1)	12(1)	22(1)	-1(1)	5(1)	-2(1)
C17	19(1)	13(1)	21(1)	-2(1)	6(1)	-1(1)
C18	17(1)	12(1)	18(1)	0(1)	6(1)	-1(1)
C19	19(1)	13(1)	19(1)	0(1)	2(1)	-3(1)
C20	18(1)	9(1)	22(1)	1(1)	2(1)	1(1)
O1	21(1)	11(1)	20(1)	0(1)	5(1)	0(1)
O2	22(1)	12(1)	23(1)	1(1)	11(1)	-1(1)
O3	15(1)	18(1)	23(1)	-3(1)	7(1)	-4(1)
O4	23(1)	10(1)	23(1)	-1(1)	10(1)	1(1)
O5	24(1)	11(1)	19(1)	0(1)	6(1)	1(1)
O6	18(1)	20(1)	19(1)	1(1)	4(1)	-3(1)

Table 5.7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5.3b**.

	x	y	z	U(eq)
H1A	8342	1661	3973	23
H1B	9156	2082	4082	23
H4A	10056	1052	5870	22
H4B	9649	218	6584	22
H5	7762	4958	4503	20
H6	8013	7696	5732	22
H7	8854	6904	7310	22
H8	9348	3367	7556	19
H9A	8140	2241	7127	22
H9B	8543	577	6653	22
H10A	7783	1318	5151	20
H10B	7368	2935	5628	20
H11A	6603	8495	503	22
H11B	5783	8036	-134	22
H14A	4917	9041	834	23
H14B	5341	9915	1930	23
H15	7228	5274	1601	20
H16A	7200	8919	2219	20
H16B	7643	7336	3095	20
H17A	6900	8019	3893	21
H17B	6467	9640	3029	21
H18	5694	6791	3215	19
H19	6207	3284	3432	22
H20	7022	2531	2622	21
H2	9067	6837	4896	27
H3	10214	4657	6056	28
H5A	5944	3294	802	27
H6A	4802	5366	890	29

Table 5.8. Torsion angles [°] for **5.3b**.

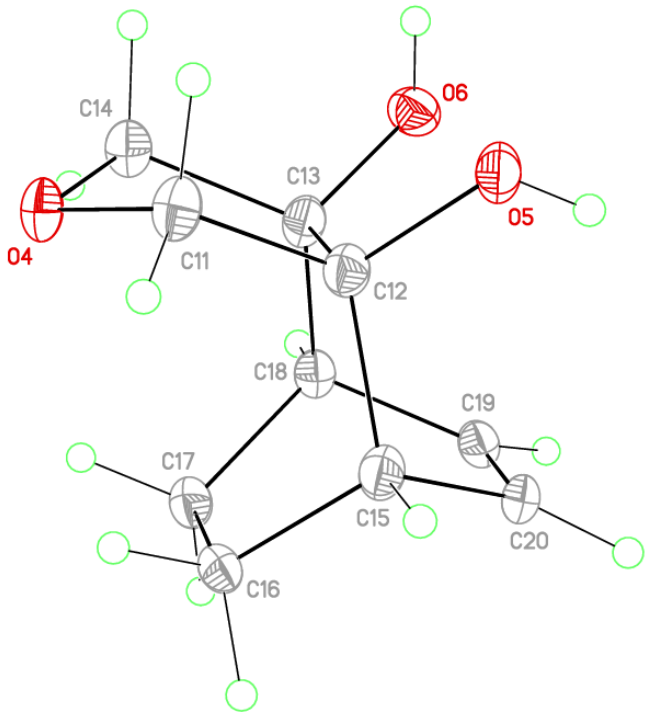
O1-C1-C2-O2	143.9(2)	O4-C11-C12-C13	24.7(2)
O1-C1-C2-C5	-93.9(2)	O5-C12-C13-O6	3.8(3)
O1-C1-C2-C3	24.6(2)	C11-C12-C13-O6	119.4(2)
O2-C2-C3-O3	4.3(3)	C15-C12-C13-O6	-119.0(2)
C1-C2-C3-O3	119.4(2)	O5-C12-C13-C14	-117.4(2)
C5-C2-C3-O3	-118.3(2)	C11-C12-C13-C14	-1.9(2)
O2-C2-C3-C4	-117.3(2)	C15-C12-C13-C14	119.8(2)
C1-C2-C3-C4	-2.2(2)	O5-C12-C13-C18	121.7(2)
C5-C2-C3-C4	120.1(2)	C11-C12-C13-C18	-122.7(2)
O2-C2-C3-C8	122.0(2)	C15-C12-C13-C18	-1.0(3)
C1-C2-C3-C8	-122.9(2)	O6-C13-C14-O4	-143.8(2)
C5-C2-C3-C8	-0.6(3)	C18-C13-C14-O4	95.7(2)
O3-C3-C4-O1	-143.9(2)	C12-C13-C14-O4	-21.4(2)
C8-C3-C4-O1	95.9(2)	O5-C12-C15-C20	-67.5(3)
C2-C3-C4-O1	-21.0(2)	C11-C12-C15-C20	171.9(2)
O2-C2-C5-C6	-67.8(3)	C13-C12-C15-C20	56.8(3)
C1-C2-C5-C6	171.7(2)	O5-C12-C15-C16	176.0(2)
C3-C2-C5-C6	56.3(3)	C11-C12-C15-C16	55.4(3)
O2-C2-C5-C10	175.7(2)	C13-C12-C15-C16	-59.6(3)
C1-C2-C5-C10	55.3(3)	C20-C15-C16-C17	-54.8(3)
C3-C2-C5-C10	-60.1(3)	C12-C15-C16-C17	61.2(3)
C10-C5-C6-C7	59.5(3)	C15-C16-C17-C18	-1.1(3)
C2-C5-C6-C7	-58.7(3)	C16-C17-C18-C19	56.4(3)
C5-C6-C7-C8	-1.1(3)	C16-C17-C18-C13	-60.1(3)
C6-C7-C8-C9	-58.2(3)	O6-C13-C18-C19	66.6(2)
C6-C7-C8-C3	60.7(3)	C14-C13-C18-C19	-169.8(2)
O3-C3-C8-C7	66.6(2)	C12-C13-C18-C19	-56.0(2)
C4-C3-C8-C7	-169.9(2)	O6-C13-C18-C17	-176.49(19)
C2-C3-C8-C7	-56.2(2)	C14-C13-C18-C17	-52.9(3)
O3-C3-C8-C9	-176.72(19)	C12-C13-C18-C17	60.9(3)
C4-C3-C8-C9	-53.2(3)	C17-C18-C19-C20	-57.9(3)
C2-C3-C8-C9	60.5(3)	C13-C18-C19-C20	60.9(3)
C7-C8-C9-C10	56.9(3)	C18-C19-C20-C15	-1.3(3)
C3-C8-C9-C10	-59.9(3)	C16-C15-C20-C19	59.4(3)
C6-C5-C10-C9	-54.8(3)	C12-C15-C20-C19	-59.0(3)
C2-C5-C10-C9	61.5(3)	C2-C1-O1-C4	-39.2(2)
C8-C9-C10-C5	-1.4(3)	C3-C4-O1-C1	37.9(2)
O4-C11-C12-O5	144.3(2)	C12-C11-O4-C14	-39.5(2)
O4-C11-C12-C15	-93.3(2)	C13-C14-O4-C11	38.3(2)

Table 5.9. Hydrogen bonds for **5.3b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C14-H14B...O6#1	0.99	2.64	3.543(3)	151.1
O2-H2...O1#2	0.84	2.12	2.920(3)	158.6
O3-H3...O2#3	0.84	1.99	2.815(3)	168.8
O5-H5A...O4#4	0.84	2.11	2.906(3)	157.8
O6-H6A...O5#5	0.84	2.01	2.838(3)	169.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 x,y+1,z #3 -x+2,-y+1,-z+1
#4 x,y-1,z #5 -x+1,-y+1,-z

Figure 5.2. View of **5.3b** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **5.3e**-CH_2Cl_2

X-ray Experimental for complex $C_{21}H_{23}NO_5$ - CH_2Cl_2: Crystals grew as thin colorless plates by slow evaporation from CH_2Cl_2/pentane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.25 x 0.06 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 1058 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 12 seconds per frame with a detector offset of +/- 41.6° and 32 seconds per frame with a detector offset of +/- 109.0°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 8. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.[29] The structure was solved by direct methods using SHELXT[30] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON[31] and WinGX.[32] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma w(|Fo|2 - |Fc|2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.1*P)^2]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.151, with R(F) equal to 0.0445 and a goodness of fit, S, = 1.07. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[33] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[34] All figures were generated using

SHELXTL/PC.[11] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.10. Crystal data and structure refinement for **5.3e**.

Empirical formula	C22 H25 Cl2 N O5	
Formula weight	454.33	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.6415(5) Å	α= 90°.
	b = 6.38976(17) Å	β= 105.433(3)°.
	c = 22.8145(6) Å	γ = 90°.
Volume	2057.46(10) $Å^3$	
Z	4	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	3.143 mm^{-1}	
F(000)	952	
Crystal size	0.250 x 0.060 x 0.030 mm^3	
Theta range for data collection	3.240 to 74.379°.	
Index ranges	-18<=h<=12, -7<=k<=7, -27<=l<=28	
Reflections collected	11749	
Independent reflections	4033 [R(int) = 0.0381]	
Completeness to theta = 67.684°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4033 / 0 / 272	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.1391	
R indices (all data)	R1 = 0.0534, wR2 = 0.1507	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.502 and -0.343 e.$Å^{-3}$	

Table 5.11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.3e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	9849(1)	1152(2)	-7618(1)	32(1)
O2	10012(1)	-4418(2)	-8846(1)	28(1)
O3	6777(1)	-1665(2)	-7839(1)	36(1)
O4	6870(1)	-5366(2)	-8315(1)	36(1)
O5	13766(1)	1063(3)	-8253(1)	33(1)
N1	10162(1)	-1548(3)	-8214(1)	24(1)
C1	9622(2)	-491(3)	-7888(1)	27(1)
C2	8713(2)	-1670(3)	-7952(1)	27(1)
C3	7884(2)	-320(3)	-8308(1)	27(1)
C4	6949(2)	-1495(3)	-8431(1)	28(1)
C5	6125(2)	-291(3)	-8857(1)	31(1)
C6	5237(2)	-1568(4)	-8915(1)	40(1)
C7	5277(2)	-3473(3)	-9139(1)	39(1)
C8	6190(2)	-3966(3)	-9298(1)	31(1)
C9	7016(2)	-3740(3)	-8716(1)	27(1)
C10	7972(2)	-4080(3)	-8853(1)	26(1)
C11	8814(2)	-3685(3)	-8303(1)	25(1)
C12	9716(2)	-3356(3)	-8494(1)	24(1)
C13	6283(2)	-106(3)	-9496(1)	29(1)
C14	6276(2)	-2319(3)	-9773(1)	30(1)
C15	11073(2)	-865(3)	-8260(1)	25(1)
C16	11175(2)	1100(3)	-8496(1)	25(1)
C17	12068(2)	1791(3)	-8515(1)	26(1)
C18	12851(2)	506(3)	-8290(1)	27(1)
C19	12740(2)	-1487(3)	-8069(1)	30(1)
C20	11853(2)	-2168(3)	-8055(1)	29(1)
C21	13921(2)	3040(4)	-8498(1)	37(1)
Cl1	12305(1)	-3421(1)	-9630(1)	45(1)
Cl2	11106(1)	36(1)	-10217(1)	41(1)
C43	11127(2)	-2489(4)	-9893(1)	36(1)

Table 5.12. Bond lengths [Å] and angles [°] for **5.3e**.

O1-C1	1.218(3)	C8-H8	1.00
O2-C12	1.217(2)	C9-C10	1.529(3)
O3-C4	1.443(2)	C10-C11	1.528(3)
O3-H3O	0.75	C10-H10A	0.99
O4-C9	1.438(2)	C10-H10B	0.99
O4-H40	0.81	C11-C12	1.511(3)
O5-C18	1.367(3)	C11-H11	1.00
O5-C21	1.423(3)	C13-C14	1.548(3)
N1-C12	1.395(3)	C13-H13A	0.99
N1-C1	1.396(3)	C13-H13B	0.99
N1-C15	1.434(3)	C14-H14A	0.99
C1-C2	1.502(3)	C14-H14B	0.99
C2-C3	1.534(3)	C15-C20	1.390(3)
C2-C11	1.544(3)	C15-C16	1.389(3)
C2-H2	1.00	C16-C17	1.392(3)
C3-C4	1.520(3)	C16-H16	0.95
C3-H3A	0.99	C17-C18	1.393(3)
C3-H3B	0.99	C17-H17	0.95
C4-C5	1.539(3)	C18-C19	1.395(3)
C4-C9	1.589(3)	C19-C20	1.379(4)
C5-C6	1.510(3)	C19-H19	0.95
C5-C13	1.541(3)	C20-H20	0.95
C5-H5	1.00	C21-H21A	0.98
C6-C7	1.328(3)	C21-H21B	0.98
C6-H6	0.95	C21-H21C	0.98
C7-C8	1.508(3)	Cl1-C43	1.771(3)
C7-H7	0.95	Cl2-C43	1.771(2)
C8-C14	1.541(3)	C43-H43A	0.99
C8-C9	1.545(3)	C43-H43B	0.99

C4-O3-H3O	111.9	C11-C2-H2	110.3
C9-O4-H40	110.5	C4-C3-C2	111.50(17)
C18-O5-C21	117.61(17)	C4-C3-H3A	109.3
C12-N1-C1	112.46(19)	C2-C3-H3A	109.3
C12-N1-C15	123.36(17)	C4-C3-H3B	109.3
C1-N1-C15	124.18(18)	C2-C3-H3B	109.3
O1-C1-N1	124.7(2)	H3A-C3-H3B	108.0
O1-C1-C2	126.7(2)	O3-C4-C3	103.77(18)
N1-C1-C2	108.56(17)	O3-C4-C5	108.98(17)
C1-C2-C3	108.97(17)	C3-C4-C5	112.70(17)
C1-C2-C11	105.29(17)	O3-C4-C9	111.14(15)
C3-C2-C11	111.45(18)	C3-C4-C9	111.79(17)
C1-C2-H2	110.3	C5-C4-C9	108.41(18)
C3-C2-H2	110.3	C6-C5-C4	107.32(19)

C6-C5-C13	107.5(2)	C14-C13-H13A	109.8
C4-C5-C13	110.24(18)	C5-C13-H13B	109.8
C6-C5-H5	110.6	C14-C13-H13B	109.8
C4-C5-H5	110.6	H13A-C13-H13B	108.3
C13-C5-H5	110.6	C8-C14-C13	109.21(17)
C7-C6-C5	113.9(2)	C8-C14-H14A	109.8
C7-C6-H6	123.1	C13-C14-H14A	109.8
C5-C6-H6	123.1	C8-C14-H14B	109.8
C6-C7-C8	114.6(2)	C13-C14-H14B	109.8
C6-C7-H7	122.7	H14A-C14-H14B	108.3
C8-C7-H7	122.7	C20-C15-C16	120.6(2)
C7-C8-C14	105.64(19)	C20-C15-N1	119.32(19)
C7-C8-C9	108.42(19)	C16-C15-N1	120.05(18)
C14-C8-C9	110.42(18)	C15-C16-C17	119.81(19)
C7-C8-H8	110.7	C15-C16-H16	120.1
C14-C8-H8	110.7	C17-C16-H16	120.1
C9-C8-H8	110.7	C16-C17-C18	119.3(2)
O4-C9-C10	109.04(17)	C16-C17-H17	120.3
O4-C9-C8	105.33(18)	C18-C17-H17	120.3
C10-C9-C8	111.21(17)	O5-C18-C17	124.5(2)
O4-C9-C4	110.83(16)	O5-C18-C19	114.96(19)
C10-C9-C4	111.78(17)	C17-C18-C19	120.5(2)
C8-C9-C4	108.47(18)	C20-C19-C18	119.9(2)
C11-C10-C9	113.06(16)	C20-C19-H19	120.1
C11-C10-H10A	109.0	C18-C19-H19	120.1
C9-C10-H10A	109.0	C19-C20-C15	119.8(2)
C11-C10-H10B	109.0	C19-C20-H20	120.1
C9-C10-H10B	109.0	C15-C20-H20	120.1
H10A-C10-H10B	107.8	O5-C21-H21A	109.5
C12-C11-C10	111.19(16)	O5-C21-H21B	109.5
C12-C11-C2	104.23(17)	H21A-C21-H21B	109.5
C10-C11-C2	113.34(18)	O5-C21-H21C	109.5
C12-C11-H11	109.3	H21A-C21-H21C	109.5
C10-C11-H11	109.3	H21B-C21-H21C	109.5
C2-C11-H11	109.3	Cl1-C43-Cl2	110.82(14)
O2-C12-N1	123.9(2)	Cl1-C43-H43A	109.5
O2-C12-C11	127.27(19)	Cl2-C43-H43A	109.5
N1-C12-C11	108.75(16)	Cl1-C43-H43B	109.5
C5-C13-C14	109.31(16)	Cl2-C43-H43B	109.5
C5-C13-H13A	109.8	H43A-C43-H43B	108.1

Table 5.13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	45(1)	26(1)	29(1)	-7(1)	16(1)	0(1)
O2	38(1)	23(1)	29(1)	-2(1)	17(1)	6(1)
O3	56(1)	23(1)	44(1)	-6(1)	42(1)	-6(1)
O4	62(1)	17(1)	42(1)	2(1)	36(1)	-5(1)
O5	29(1)	37(1)	34(1)	1(1)	11(1)	8(1)
N1	34(1)	21(1)	22(1)	1(1)	13(1)	4(1)
C1	41(1)	23(1)	20(1)	1(1)	14(1)	4(1)
C2	46(1)	19(1)	25(1)	-1(1)	23(1)	3(1)
C3	41(1)	14(1)	35(1)	-2(1)	25(1)	-1(1)
C4	40(1)	17(1)	38(1)	-4(1)	31(1)	-1(1)
C5	36(1)	15(1)	53(1)	-4(1)	32(1)	-1(1)
C6	38(1)	27(1)	69(2)	-4(1)	39(1)	-6(1)
C7	40(1)	22(1)	66(2)	-5(1)	34(1)	-7(1)
C8	38(1)	17(1)	46(1)	-5(1)	25(1)	-2(1)
C9	44(1)	13(1)	36(1)	1(1)	28(1)	-3(1)
C10	38(1)	18(1)	28(1)	-1(1)	21(1)	2(1)
C11	42(1)	15(1)	25(1)	1(1)	19(1)	3(1)
C12	38(1)	17(1)	20(1)	3(1)	13(1)	6(1)
C13	28(1)	18(1)	46(1)	2(1)	18(1)	-4(1)
C14	31(1)	24(1)	39(1)	-3(1)	18(1)	2(1)
C15	33(1)	24(1)	19(1)	-1(1)	9(1)	4(1)
C16	29(1)	25(1)	21(1)	3(1)	6(1)	6(1)
C17	32(1)	24(1)	22(1)	0(1)	7(1)	6(1)
C18	30(1)	32(1)	20(1)	-2(1)	8(1)	7(1)
C19	38(1)	29(1)	23(1)	1(1)	9(1)	15(1)
C20	41(1)	25(1)	21(1)	3(1)	10(1)	9(1)
C21	30(1)	36(1)	42(1)	-6(1)	4(1)	-3(1)
Cl1	55(1)	50(1)	31(1)	4(1)	14(1)	20(1)
Cl2	38(1)	47(1)	44(1)	17(1)	21(1)	7(1)
C43	41(1)	36(1)	37(1)	6(1)	20(1)	1(1)

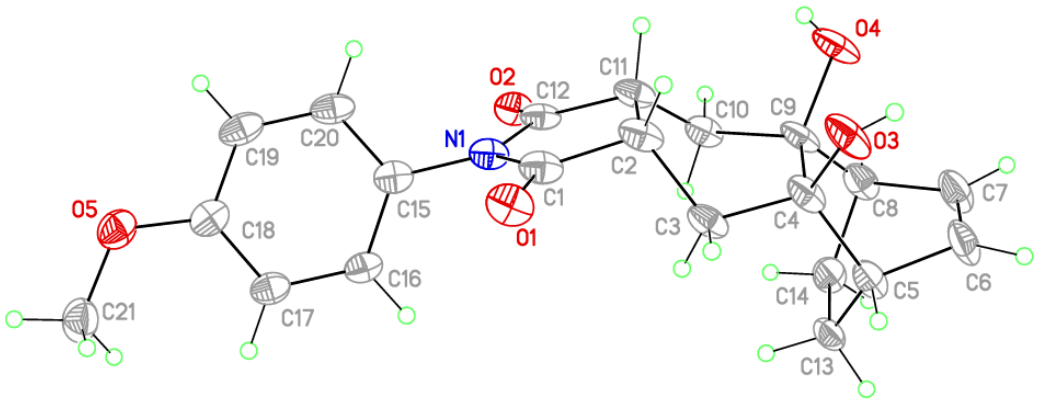
Table 5.14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5.3e**.

	x	y	z	U(eq)
H3O	6369	-2384	-7843	54
H40	7297	-5380	-8007	54
H2	8630	-2026	-7542	33
H3A	7845	965	-8073	32
H3B	7999	105	-8699	32
H5	6057	1127	-8687	37
H6	4699	-1055	-8802	48
H7	4771	-4447	-9196	47
H8	6173	-5411	-9469	37
H10A	8004	-5536	-8994	31
H10B	8019	-3132	-9187	31
H11	8895	-4910	-8021	30
H13A	6898	584	-9469	35
H13B	5774	757	-9759	35
H14A	5735	-2451	-10139	36
H14B	6868	-2548	-9896	36
H16	10636	1970	-8643	30
H17	12142	3125	-8680	31
H19	13275	-2372	-7929	36
H20	11774	-3525	-7904	34
H21A	13576	3096	-8930	56
H21B	14600	3228	-8455	56
H21C	13693	4156	-8278	56
H43A	10833	-2432	-9550	44
H43B	10753	-3466	-10202	44

Table 5.15. Torsion angles [°] for **5.3e**.

C12-N1-C1-O1	-178.05(19)	C1-C2-C11-C12	-8.1(2)
C15-N1-C1-O1	2.0(3)	C3-C2-C11-C12	109.95(19)
C12-N1-C1-C2	-0.5(2)	C1-C2-C11-C10	-129.09(18)
C15-N1-C1-C2	179.49(17)	C3-C2-C11-C10	-11.1(2)
O1-C1-C2-C3	63.4(3)	C1-N1-C12-O2	173.03(18)
N1-C1-C2-C3	-114.10(18)	C15-N1-C12-O2	-7.0(3)
O1-C1-C2-C11	-177.0(2)	C1-N1-C12-C11	-4.9(2)
N1-C1-C2-C11	5.6(2)	C15-N1-C12-C11	175.04(17)
C1-C2-C3-C4	175.57(16)	C10-C11-C12-O2	-47.4(3)
C11-C2-C3-C4	59.8(2)	C2-C11-C12-O2	-169.85(19)
C2-C3-C4-O3	69.6(2)	C10-C11-C12-N1	130.50(17)
C2-C3-C4-C5	-172.63(16)	C2-C11-C12-N1	8.0(2)
C2-C3-C4-C9	-50.2(2)	C6-C5-C13-C14	-53.1(2)
O3-C4-C5-C6	-62.6(2)	C4-C5-C13-C14	63.6(2)
C3-C4-C5-C6	-177.18(17)	C7-C8-C14-C13	59.1(2)
C9-C4-C5-C6	58.5(2)	C9-C8-C14-C13	-58.0(2)
O3-C4-C5-C13	-179.30(16)	C5-C13-C14-C8	-4.3(3)
C3-C4-C5-C13	66.1(2)	C12-N1-C15-C20	-59.6(3)
C9-C4-C5-C13	-58.2(2)	C1-N1-C15-C20	120.4(2)
C4-C5-C6-C7	-59.5(3)	C12-N1-C15-C16	121.9(2)
C13-C5-C6-C7	59.0(3)	C1-N1-C15-C16	-58.1(3)
C5-C6-C7-C8	-0.8(4)	C20-C15-C16-C17	-1.3(3)
C6-C7-C8-C14	-59.3(3)	N1-C15-C16-C17	177.26(17)
C6-C7-C8-C9	59.1(3)	C15-C16-C17-C18	-0.8(3)
C7-C8-C9-O4	65.7(2)	C21-O5-C18-C17	-4.3(3)
C14-C8-C9-O4	-178.99(16)	C21-O5-C18-C19	177.09(18)
C7-C8-C9-C10	-176.30(16)	C16-C17-C18-O5	-176.07(18)
C14-C8-C9-C10	-61.0(2)	C16-C17-C18-C19	2.5(3)
C7-C8-C9-C4	-53.0(2)	O5-C18-C19-C20	176.61(18)
C14-C8-C9-C4	62.3(2)	C17-C18-C19-C20	-2.1(3)
O3-C4-C9-O4	1.0(3)	C18-C19-C20-C15	0.0(3)
C3-C4-C9-O4	116.4(2)	C16-C15-C20-C19	1.7(3)
C5-C4-C9-O4	-118.8(2)	N1-C15-C20-C19	-176.84(18)
O3-C4-C9-C10	-120.9(2)		
C3-C4-C9-C10	-5.4(2)		
C5-C4-C9-C10	119.38(19)		
O3-C4-C9-C8	116.2(2)		
C3-C4-C9-C8	-128.41(19)		
C5-C4-C9-C8	-3.6(2)		
O4-C9-C10-C11	-69.3(2)		
C8-C9-C10-C11	175.00(16)		
C4-C9-C10-C11	53.6(2)		
C9-C10-C11-C12	-161.89(16)		
C9-C10-C11-C2	-44.9(2)		

Figure 5.3. View of **5.3e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **5.3d'**-$CHCl_3$

X-ray Experimental for $C_{24}H_{26}O_2$: Crystals grew as large, colorless prisms by vapor diffusion of pentane in a chloroform solution. The data crystal was cut from a larger crystal and had approximate dimensions; 0.20 x 0.15 x 0.14 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1616 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 40 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 14. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[37] The structure was solved by direct methods using SuperFlip[38] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[39] Structure analysis was aided by use of the programs PLATON98[40] and WinGX.[33] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom. The hydrogen atoms bound to oxygen were located in a ΔF map and refined with isotropic displacement parameters. The function, $\Sigma w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.052*P)^2 + (0.2753*P)]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. Rw(F2) refined to 0.100, with R(F) equal to 0.0365 and a goodness of fit, S, = 1.06. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[10] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[35] All figures were generated using SHELXTL/PC.[36] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.16. Crystal data and structure refinement for **5.3d'**.

Empirical formula	C24 H26 O2	
Formula weight	346.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.5662(12) Å	α= 74.401(4)°.
	b = 9.1574(14) Å	β= 88.397(4)°.
	c = 13.690(2) Å	γ = 78.227(4)°.
Volume	894.0(2) $Å^3$	
Z	2	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	372	
Crystal size	0.200 x 0.150 x 0.140 mm^3	
Theta range for data collection	3.091 to 27.474°.	
Index ranges	-9<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected	16800	
Independent reflections	4075 [R(int) = 0.0260]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.860	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4075 / 156 / 243	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0976	
R indices (all data)	R1 = 0.0414, wR2 = 0.1005	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.349 and -0.200 $e.Å^{-3}$	

Table 5.17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.3d'**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	2867(1)	4512(1)	1313(1)	14(1)
C2	2939(1)	2928(1)	1149(1)	15(1)
C3	1692(2)	2329(1)	756(1)	19(1)
C4	2182(2)	766(1)	709(1)	22(1)
C5	3851(2)	-154(1)	1030(1)	21(1)
C6	5171(2)	451(1)	1419(1)	17(1)
C7	6985(2)	-304(1)	1730(1)	20(1)
C8	8132(2)	481(1)	2041(1)	20(1)
C9	7568(1)	2037(1)	2093(1)	17(1)
C10	5814(1)	2777(1)	1825(1)	14(1)
C11	4799(1)	4397(1)	1803(1)	14(1)
C12	4653(1)	1994(1)	1474(1)	14(1)
C13	1384(1)	4959(1)	2040(1)	16(1)
C14	1676(2)	6419(1)	2266(1)	19(1)
C15	3273(2)	6281(1)	2699(1)	19(1)
C16	4484(1)	4699(1)	2859(1)	15(1)
C17	3506(1)	3473(1)	3544(1)	13(1)
C18	3589(1)	3536(1)	4655(1)	17(1)
C19	3768(2)	1948(1)	5424(1)	20(1)
C20	2339(2)	1035(1)	5318(1)	19(1)
C21	393(2)	1851(1)	5441(1)	19(1)
C22	-700(1)	2667(1)	4450(1)	19(1)
C23	-87(1)	4042(1)	3707(1)	16(1)
C24	1576(1)	3666(1)	3065(1)	14(1)
O1	2601(1)	5654(1)	345(1)	19(1)
O2	5685(1)	5577(1)	1225(1)	18(1)

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Table 5.18. Bond lengths [Å] and angles [°] for **5.3d'**.

C1-O1	1.4404(12)	C15-C16	1.5116(14)
C1-C2	1.5157(14)	C15-H15	0.95
C1-C13	1.5443(14)	C16-C17	1.5567(13)
C1-C11	1.5978(14)	C16-H16	1.00
C2-C3	1.3710(15)	C17-C18	1.5410(14)
C2-C12	1.4089(14)	C17-C24	1.5742(14)
C3-C4	1.4224(16)	C17-H17	1.00
C3-H3	0.95	C18-C19	1.5305(15)
C4-C5	1.3766(17)	C18-H18A	0.99
C4-H4	0.95	C18-H18B	0.99
C5-C6	1.4160(16)	C19-C20	1.5274(15)
C5-H5	0.95	C19-H19A	0.99
C6-C12	1.4089(14)	C19-H19B	0.99
C6-C7	1.4241(16)	C20-C21	1.5360(15)
C7-C8	1.3746(16)	C20-H20A	0.99
C7-H7	0.95	C20-H20B	0.99
C8-C9	1.4223(15)	C21-C22	1.5324(15)
C8-H8	0.95	C21-H21A	0.99
C9-C10	1.3719(14)	C21-H21B	0.99
C9-H9	0.95	C22-C23	1.5358(14)
C10-C12	1.4082(14)	C22-H22A	0.99
C10-C11	1.5185(14)	C22-H22B	0.99
C11-O2	1.4311(12)	C23-C24	1.5486(14)
C11-C16	1.5461(14)	C23-H23A	0.99
C13-C14	1.5091(15)	C23-H23B	0.99
C13-C24	1.5623(14)	C24-H24	1.00
C13-H13	1.00	O1-H1O	0.885(18)
C14-C15	1.3291(17)	O2-H2O	0.90(2)
C14-H14	0.95		

O1-C1-C2	108.86(8)	C3-C4-H4	118.6
O1-C1-C13	109.75(8)	C4-C5-C6	120.04(10)
C2-C1-C13	113.83(8)	C4-C5-H5	120.0
O1-C1-C11	110.58(8)	C6-C5-H5	120.0
C2-C1-C11	104.73(8)	C12-C6-C5	116.31(10)
C13-C1-C11	108.99(8)	C12-C6-C7	116.22(10)
C3-C2-C12	119.34(10)	C5-C6-C7	127.43(10)
C3-C2-C1	131.81(10)	C8-C7-C6	120.16(10)
C12-C2-C1	108.85(9)	C8-C7-H7	119.9
C2-C3-C4	118.06(10)	C6-C7-H7	119.9
C2-C3-H3	121.0	C7-C8-C9	122.39(10)
C4-C3-H3	121.0	C7-C8-H8	118.8
C5-C4-C3	122.82(10)	C9-C8-H8	118.8
C5-C4-H4	118.6	C10-C9-C8	118.62(10)

C10-C9-H9	120.7	C19-C18-H18B	108.9
C8-C9-H9	120.7	C17-C18-H18B	108.9
C9-C10-C12	119.10(9)	H18A-C18-H18B	107.7
C9-C10-C11	131.67(10)	C20-C19-C18	115.36(9)
C12-C10-C11	109.21(9)	C20-C19-H19A	108.4
O2-C11-C10	112.64(8)	C18-C19-H19A	108.4
O2-C11-C16	106.47(8)	C20-C19-H19B	108.4
C10-C11-C16	114.64(8)	C18-C19-H19B	108.4
O2-C11-C1	111.55(8)	H19A-C19-H19B	107.5
C10-C11-C1	103.97(8)	C19-C20-C21	114.26(9)
C16-C11-C1	107.54(8)	C19-C20-H20A	108.7
C10-C12-C2	113.11(9)	C21-C20-H20A	108.7
C10-C12-C6	123.44(10)	C19-C20-H20B	108.7
C2-C12-C6	123.41(10)	C21-C20-H20B	108.7
C14-C13-C1	107.70(8)	H20A-C20-H20B	107.6
C14-C13-C24	107.61(8)	C22-C21-C20	115.42(9)
C1-C13-C24	110.13(8)	C22-C21-H21A	108.4
C14-C13-H13	110.4	C20-C21-H21A	108.4
C1-C13-H13	110.4	C22-C21-H21B	108.4
C24-C13-H13	110.4	C20-C21-H21B	108.4
C15-C14-C13	114.21(9)	H21A-C21-H21B	107.5
C15-C14-H14	122.9	C21-C22-C23	118.90(9)
C13-C14-H14	122.9	C21-C22-H22A	107.6
C14-C15-C16	114.19(9)	C23-C22-H22A	107.6
C14-C15-H15	122.9	C21-C22-H22B	107.6
C16-C15-H15	122.9	C23-C22-H22B	107.6
C15-C16-C11	107.18(8)	H22A-C22-H22B	107.0
C15-C16-C17	108.61(8)	C22-C23-C24	117.13(9)
C11-C16-C17	110.21(8)	C22-C23-H23A	108.0
C15-C16-H16	110.3	C24-C23-H23A	108.0
C11-C16-H16	110.3	C22-C23-H23B	108.0
C17-C16-H16	110.3	C24-C23-H23B	108.0
C18-C17-C16	109.93(8)	H23A-C23-H23B	107.3
C18-C17-C24	116.84(8)	C23-C24-C13	108.36(8)
C16-C17-C24	108.87(8)	C23-C24-C17	117.92(8)
C18-C17-H17	106.9	C13-C24-C17	108.22(8)
C16-C17-H17	106.9	C23-C24-H24	107.3
C24-C17-H17	106.9	C13-C24-H24	107.3
C19-C18-C17	113.40(8)	C17-C24-H24	107.3
C19-C18-H18A	108.9	C1-O1-H1O	104.0(12)
C17-C18-H18A	108.9	C11-O2-H2O	108.2(13)

Table 5.19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5.3d'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	14(1)	14(1)	13(1)	-1(1)	2(1)	-2(1)
C2	15(1)	17(1)	12(1)	-3(1)	4(1)	-4(1)
C3	16(1)	28(1)	16(1)	-7(1)	3(1)	-7(1)
C4	25(1)	30(1)	19(1)	-12(1)	7(1)	-16(1)
C5	29(1)	19(1)	18(1)	-7(1)	9(1)	-10(1)
C6	23(1)	15(1)	13(1)	-3(1)	6(1)	-4(1)
C7	26(1)	14(1)	16(1)	-3(1)	6(1)	1(1)
C8	18(1)	22(1)	15(1)	-2(1)	2(1)	4(1)
C9	15(1)	21(1)	13(1)	-4(1)	2(1)	-4(1)
C10	15(1)	14(1)	11(1)	-2(1)	4(1)	-3(1)
C11	14(1)	13(1)	15(1)	-2(1)	4(1)	-4(1)
C12	16(1)	15(1)	11(1)	-3(1)	4(1)	-4(1)
C13	13(1)	15(1)	16(1)	-2(1)	2(1)	0(1)
C14	21(1)	12(1)	21(1)	-2(1)	7(1)	0(1)
C15	24(1)	13(1)	21(1)	-6(1)	8(1)	-6(1)
C16	15(1)	14(1)	16(1)	-5(1)	3(1)	-5(1)
C17	14(1)	13(1)	14(1)	-4(1)	3(1)	-3(1)
C18	17(1)	20(1)	16(1)	-7(1)	3(1)	-7(1)
C19	20(1)	24(1)	15(1)	-3(1)	0(1)	-5(1)
C20	22(1)	16(1)	16(1)	-2(1)	3(1)	-4(1)
C21	22(1)	18(1)	16(1)	-4(1)	5(1)	-7(1)
C22	16(1)	20(1)	19(1)	-4(1)	5(1)	-6(1)
C23	14(1)	16(1)	18(1)	-4(1)	4(1)	-2(1)
C24	14(1)	13(1)	15(1)	-3(1)	3(1)	-3(1)
O1	20(1)	17(1)	15(1)	2(1)	1(1)	-2(1)
O2	21(1)	16(1)	19(1)	-4(1)	8(1)	-8(1)

Table 5.20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5.3d'**.

	x	y	z	U(eq)
H3	534	2941	522	23
H4	1320	338	445	27
H5	4117	-1195	989	25
H7	7402	-1352	1722	24
H8	9345	-36	2228	24
H9	8389	2553	2310	20
H13	159	5132	1721	19
H14	793	7355	2112	23
H15	3624	7106	2891	23
H16	5661	4672	3186	18
H17	4205	2433	3519	16
H18A	4630	3989	4752	20
H18B	2479	4229	4792	20
H19A	4974	1319	5358	24
H19B	3717	2096	6115	24
H20A	2603	21	5833	22
H20B	2432	834	4641	22
H21A	-253	1074	5859	22
H21B	432	2626	5819	22
H22A	-1957	3035	4631	22
H22B	-732	1880	4081	22
H23A	182	4738	4101	20
H23B	-1114	4628	3236	20
H24	1527	2674	2902	16
H1O	3260(20)	6330(20)	400(13)	44(5)
H2O	6280(30)	5230(20)	728(15)	56(5)

Table 5.21. Torsion angles [°] for **5.3d'**.

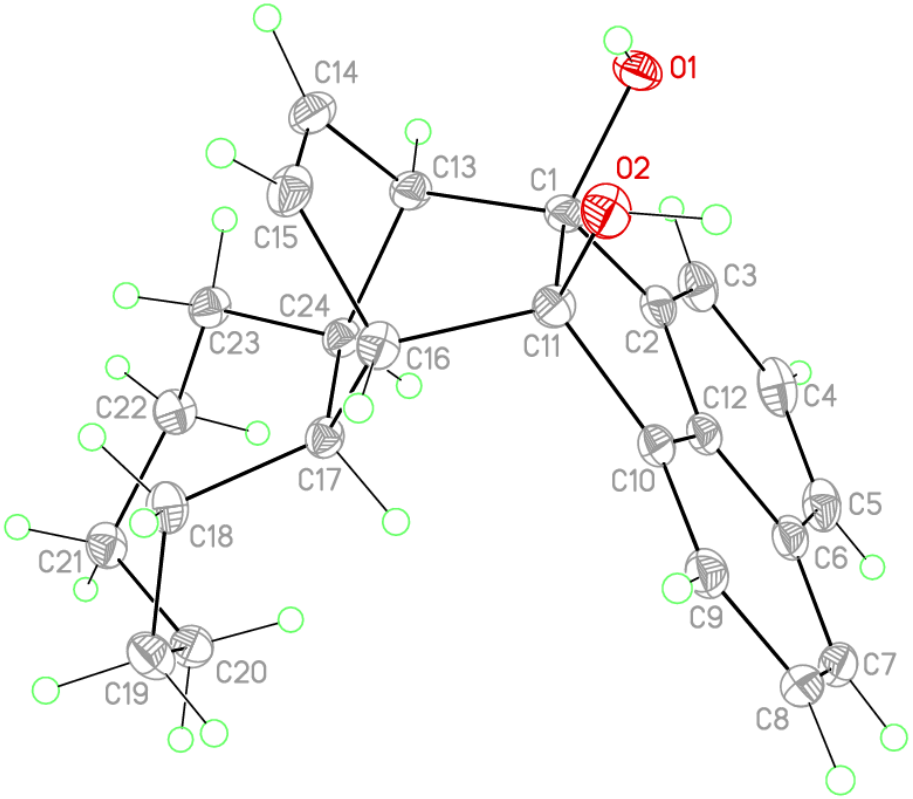
O1-C1-C2-C3	-61.80(14)	C7-C6-C12-C10	-0.93(14)
C13-C1-C2-C3	60.96(14)	C5-C6-C12-C2	-1.07(15)
C11-C1-C2-C3	179.91(10)	C7-C6-C12-C2	176.82(9)
O1-C1-C2-C12	117.56(9)	O1-C1-C13-C14	-67.07(11)
C13-C1-C2-C12	-119.68(9)	C2-C1-C13-C14	170.65(8)
C11-C1-C2-C12	-0.73(10)	C11-C1-C13-C14	54.16(10)
C12-C2-C3-C4	1.01(15)	O1-C1-C13-C24	175.84(8)
C1-C2-C3-C4	-179.68(10)	C2-C1-C13-C24	53.57(11)
C2-C3-C4-C5	-0.72(16)	C11-C1-C13-C24	-62.92(10)
C3-C4-C5-C6	-0.50(16)	C1-C13-C14-C15	-59.80(12)
C4-C5-C6-C12	1.35(15)	C24-C13-C14-C15	58.91(11)
C4-C5-C6-C7	-176.27(10)	C13-C14-C15-C16	1.03(13)
C12-C6-C7-C8	-1.24(14)	C14-C15-C16-C11	59.93(11)
C5-C6-C7-C8	176.38(10)	C14-C15-C16-C17	-59.13(12)
C6-C7-C8-C9	1.68(16)	O2-C11-C16-C15	61.51(10)
C7-C8-C9-C10	0.11(15)	C10-C11-C16-C15	-173.24(8)
C8-C9-C10-C12	-2.22(14)	C1-C11-C16-C15	-58.18(10)
C8-C9-C10-C11	179.48(10)	O2-C11-C16-C17	179.53(8)
C9-C10-C11-O2	53.93(14)	C10-C11-C16-C17	-55.22(11)
C12-C10-C11-O2	-124.49(9)	C1-C11-C16-C17	59.85(10)
C9-C10-C11-C16	-68.02(14)	C15-C16-C17-C18	-75.97(10)
C12-C10-C11-C16	113.55(9)	C11-C16-C17-C18	166.89(8)
C9-C10-C11-C1	174.86(10)	C15-C16-C17-C24	53.19(10)
C12-C10-C11-C1	-3.57(10)	C11-C16-C17-C24	-63.95(10)
O1-C1-C11-O2	7.09(11)	C16-C17-C18-C19	-144.88(9)
C2-C1-C11-O2	124.20(8)	C24-C17-C18-C19	90.44(11)
C13-C1-C11-O2	-113.64(9)	C17-C18-C19-C20	-53.88(12)
O1-C1-C11-C10	-114.56(8)	C18-C19-C20-C21	-60.20(12)
C2-C1-C11-C10	2.55(9)	C19-C20-C21-C22	100.45(11)
C13-C1-C11-C10	124.71(8)	C20-C21-C22-C23	-64.10(13)
O1-C1-C11-C16	123.48(8)	C21-C22-C23-C24	75.68(13)
C2-C1-C11-C16	-119.41(8)	C22-C23-C24-C13	150.73(9)
C13-C1-C11-C16	2.76(10)	C22-C23-C24-C17	-85.99(11)
C9-C10-C12-C2	-175.25(9)	C14-C13-C24-C23	70.97(10)
C11-C10-C12-C2	3.40(11)	C1-C13-C24-C23	-171.89(8)
C9-C10-C12-C6	2.71(15)	C14-C13-C24-C17	-57.97(10)
C11-C10-C12-C6	-178.64(9)	C1-C13-C24-C17	59.16(10)
C3-C2-C12-C10	177.84(9)	C18-C17-C24-C23	5.11(13)
C1-C2-C12-C10	-1.62(11)	C16-C17-C24-C23	-120.11(9)
C3-C2-C12-C6	-0.13(15)	C18-C17-C24-C13	128.46(9)
C1-C2-C12-C6	-179.58(9)	C16-C17-C24-C13	3.24(10)
C5-C6-C12-C10	-178.82(9)		

Table 5.22. Hydrogen bonds for **5.3d'** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1O...O2	0.885(18)	2.076(18)	2.6350(12)	120.2(15)
O2-H2O...O1#1	0.90(2)	1.96(2)	2.8494(11)	174.3(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Figure 5.4. View of **5.3d'** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **5.4c**-CH_2Cl_2

X-ray Experimental for $C_{16}H_{16}O_2$ - 1/8 C_5H_{12} - 1/8 CH_2Cl_2: Crystals grew as clusters of colorless prisms by vapor diffusion of pentane into a dichloromethane solution. The data crystal was cut from a larger crystal and had approximate dimensions; 0.40 x 0.30 x 0.25 mm. The data were collected on a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD using a graphite monochromator with MoKα radiation (λ = 0.71075Å). A total of 469 frames of data were collected using ω-scans with a scan range of 1˚and a counting time of 60 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 21. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[37] The structure was solved by direct methods using SIR2004[17] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[39] Structure analysis was aided by use of the programs PLATON98[40] and WinGX[33] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on the hydroxyl oxygen atoms were observed in a ΔF map and refined with isotropic displacement parameters.
Both a molecule of dichloromethane and a molecule of n-pentane were disordered around a crystallographic inversion center. The dichloromethane was disordered around an inversion center at 1/2, 0, 1/2, while the n-pentane molecule was disordered around an inversion center at 0, 1, 0. In each case, the site occupancy factors were set to 1/2. For pentane, the C-C bond and the C-C-C bond angles were restrained to be equivalent. For DCM, the C-Cl bond lengths were restrained to be equivalent and the Cl...Cl distance was restrained to be approximately 2.95Å in order to

maintain a Cl-C-Cl bond angle close to 109 degrees. The DCM molecule was located near an inversion center in such a manner that the carbon atom resided very near where a Cl atom of the symmetry related molecule resided. As a result, the displacement parameter for the carbon atom was highly correlated to that of the Cl atom. In the final refinement model, the isotropic displacement parameter for the carbon atom, C1b, was tied to be 1.2 times the Ueq for Cl2.

The function, $\sum w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.0705*P)^2 + (2.1979*P)]$ and $P = (|Fo|^2 + 2|Fc|2)/3$. Rw(F2) refined to 0.148, with R(F) equal to 0.0543 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[34] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[35] All figures were generated using SHELXTL/PC.[36] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.23. Crystal data and structure refinement for **5.4c**.

Empirical formula	C16.75 H17.75 Cl0.25 O2	
Formula weight	259.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.728(4) Å	α= 79.921(7)°.
	b = 11.923(4) Å	β= 79.758(7)°.
	c = 19.838(7) Å	γ = 77.926(8)°.
Volume	2642.1(16) $Å^3$	
Z	8	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.133 mm^{-1}	
F(000)	1108	
Crystal size	0.400 x 0.300 x 0.250 mm	
Theta range for data collection	3.163 to 27.447°.	
Index ranges	-15<=h<=15, -15<=k<=15, -25<=l<=25	
Reflections collected	24332	
Independent reflections	11921 [R(int) = 0.0267]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.874	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11921 / 36 / 749	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1393	
R indices (all data)	R1 = 0.0644, wR2 = 0.1481	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.511 and -0.712 $e.Å^{-3}$	

Table 5.24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.4c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	6663(1)	5901(1)	3237(1)	21(1)
O2	8454(1)	6018(1)	2136(1)	20(1)
C1	6778(2)	7061(1)	2937(1)	17(1)
C2	5591(2)	7679(2)	2689(1)	21(1)
C3	5882(2)	8041(1)	1918(1)	20(1)
C4	5107(2)	8600(2)	1450(1)	26(1)
C5	5548(2)	8795(2)	750(1)	32(1)
C6	6746(2)	8458(2)	515(1)	32(1)
C7	7526(2)	7917(2)	981(1)	25(1)
C8	7082(2)	7712(1)	1683(1)	19(1)
C9	7770(2)	7122(1)	2269(1)	17(1)
C10	8568(2)	7865(2)	2453(1)	21(1)
C11	9268(2)	7170(2)	3019(1)	24(1)
C12	8343(2)	7078(2)	3661(1)	24(1)
C13	7187(2)	7726(2)	3420(1)	20(1)
C14	7706(2)	8712(2)	2914(1)	21(1)
C15	8504(2)	9118(2)	3323(1)	27(1)
C16	9174(2)	7932(2)	3576(1)	27(1)
O3	7427(1)	4687(1)	1456(1)	17(1)
O4	6544(1)	3828(1)	2782(1)	18(1)
C17	6297(1)	4373(1)	1509(1)	15(1)
C18	5420(1)	5483(1)	1271(1)	18(1)
C19	4434(1)	5630(1)	1875(1)	18(1)
C20	3413(2)	6481(2)	1918(1)	23(1)
C21	2599(2)	6443(2)	2521(1)	27(1)
C22	2796(2)	5575(2)	3081(1)	27(1)
C23	3820(2)	4730(2)	3045(1)	22(1)
C24	4631(1)	4765(1)	2436(1)	17(1)
C25	5773(1)	3910(1)	2285(1)	15(1)
C26	5567(2)	2699(1)	2232(1)	18(1)
C27	6744(2)	1868(1)	2088(1)	19(1)
C28	7240(2)	2304(1)	1345(1)	19(1)
C29	6317(1)	3354(1)	1120(1)	17(1)
C30	5210(2)	2849(1)	1498(1)	19(1)
C31	5419(2)	1612(2)	1320(1)	24(1)
C32	6666(2)	1232(2)	1500(1)	22(1)
O5	8304(1)	2164(1)	3339(1)	20(1)
O6	8548(1)	4231(1)	3682(1)	25(1)
C33	8533(2)	2074(2)	4032(1)	20(1)
C34	9688(2)	1174(2)	4110(1)	21(1)
C35	10534(2)	1822(2)	4311(1)	23(1)

C36	11704(2)	1420(2)	4417(1)	32(1)
C37	12357(2)	2206(2)	4539(1)	40(1)
C38	11852(2)	3369(2)	4556(1)	38(1)
C39	10683(2)	3770(2)	4459(1)	30(1)
C40	10025(2)	2987(2)	4343(1)	24(1)
C41	8758(2)	3262(2)	4211(1)	22(1)
C42	7857(2)	3465(2)	4865(1)	30(1)
C43	6605(2)	3798(2)	4677(1)	35(1)
C44	6363(2)	2681(2)	4492(1)	28(1)
C45	7496(2)	1796(2)	4592(1)	22(1)
C46	7760(2)	2218(2)	5240(1)	28(1)
C47	6576(2)	2368(2)	5723(1)	36(1)
C48	5827(2)	3069(2)	5193(1)	37(1)
O7	10408(1)	4441(1)	2624(1)	18(1)
O8	9280(1)	3196(1)	2001(1)	18(1)
C49	11206(1)	3693(1)	2186(1)	15(1)
C50	12020(2)	2801(2)	2637(1)	18(1)
C51	11896(2)	1626(2)	2499(1)	19(1)
C52	12479(2)	531(2)	2764(1)	24(1)
C53	12202(2)	-456(2)	2594(1)	28(1)
C54	11359(2)	-360(2)	2159(1)	29(1)
C55	10786(2)	730(2)	1884(1)	23(1)
C56	11065(1)	1720(1)	2058(1)	17(1)
C57	10538(1)	2975(1)	1824(1)	15(1)
C58	10884(1)	3380(2)	1048(1)	17(1)
C59	10366(2)	4666(2)	851(1)	18(1)
C60	11055(2)	5314(2)	1193(1)	18(1)
C61	11896(1)	4355(1)	1567(1)	16(1)
C62	12189(1)	3529(2)	1004(1)	18(1)
C63	12441(2)	4317(2)	318(1)	22(1)
C64	11351(2)	5252(2)	423(1)	21(1)
C1A	1254(7)	8451(6)	442(4)	59(2)
C2A	959(5)	9721(5)	98(3)	52(2)
C3A	-355(4)	10015(5)	46(3)	48(2)
C4A	-681(6)	11253(5)	-356(3)	49(2)
C5A	-2042(7)	11488(6)	-371(3)	61(2)
Cl1	5041(1)	556(1)	3857(1)	43(1)
Cl2	4820(1)	260(2)	5383(1)	38(1)
C1B	5493(8)	-338(8)	4616(4)	45

Table 5.25. Bond lengths [Å] and angles [°] for **5.4c**.

O1-C1	1.431(2)	C17-C18	1.555(2)
O1-H1O	0.86(3)	C17-C25	1.600(2)
O2-C9	1.432(2)	C18-C19	1.517(2)
O2-H2O	0.84(3)	C18-H18A	0.99
C1-C13	1.539(2)	C18-H18B	0.99
C1-C2	1.552(3)	C19-C24	1.396(2)
C1-C9	1.603(2)	C19-C20	1.398(2)
C2-C3	1.513(2)	C20-C21	1.392(3)
C2-H2A	0.99	C20-H20	0.95
C2-H2B	0.99	C21-C22	1.397(3)
C3-C8	1.397(3)	C21-H21	0.95
C3-C4	1.401(3)	C22-C23	1.397(3)
C4-C5	1.390(3)	C22-H22	0.95
C4-H4	0.95	C23-C24	1.398(2)
C5-C6	1.396(3)	C23-H23	0.95
C5-H5	0.95	C24-C25	1.522(2)
C6-C7	1.398(3)	C25-C26	1.537(2)
C6-H6	0.95	C26-C27	1.534(2)
C7-C8	1.395(2)	C26-C30	1.557(2)
C7-H7	0.95	C26-H26	1.00
C8-C9	1.518(2)	C27-C32	1.524(2)
C9-C10	1.542(2)	C27-C28	1.528(2)
C10-C11	1.529(3)	C27-H27	1.00
C10-C14	1.563(2)	C28-C32	1.527(2)
C10-H10	1.00	C28-C29	1.532(2)
C11-C12	1.524(3)	C28-H28	1.00
C11-C16	1.525(2)	C29-C30	1.560(2)
C11-H11	1.00	C29-H29	1.00
C12-C16	1.520(3)	C30-C31	1.536(2)
C12-C13	1.525(3)	C30-H30	1.00
C12-H12	1.00	C31-C32	1.523(3)
C13-C14	1.559(2)	C31-H31A	0.99
C13-H13	1.00	C31-H31B	0.99
C14-C15	1.539(3)	C32-H32	1.00
C14-H14	1.00	O5-C33	1.428(2)
C15-C16	1.515(3)	O5-H5O	0.88(3)
C15-H15A	0.99	O6-C41	1.430(2)
C15-H15B	0.99	O6-H6O	0.83(3)
C16-H16	1.00	C33-C45	1.544(2)
O3-C17	1.4320(19)	C33-C34	1.555(2)
O3-H3O	0.81(3)	C33-C41	1.604(2)
O4-C25	1.430(2)	C34-C35	1.519(2)
O4-H4O	0.79(2)	C34-H34A	0.99
C17-C29	1.543(2)	C34-H34B	0.99

C35-C36	1.397(3)	C53-H53	0.95
C35-C40	1.399(3)	C54-C55	1.398(3)
C36-C37	1.404(3)	C54-H54	0.95
C36-H36	0.95	C55-C56	1.401(2)
C37-C38	1.393(3)	C55-H55	0.95
C37-H37	0.95	C56-C57	1.519(2)
C38-C39	1.390(3)	C57-C58	1.539(2)
C38-H38	0.95	C58-C59	1.535(2)
C39-C40	1.401(3)	C58-C62	1.563(2)
C39-H39	0.95	C58-H58	1.00
C40-C41	1.513(3)	C59-C64	1.526(2)
C41-C42	1.540(2)	C59-C60	1.532(2)
C42-C43	1.533(3)	C59-H59	1.00
C42-C46	1.560(3)	C60-C64	1.517(2)
C42-H42	1.00	C60-C61	1.525(2)
C43-C48	1.524(3)	C60-H60	1.00
C43-C44	1.535(3)	C61-C62	1.563(2)
C43-H43	1.00	C61-H61	1.00
C44-C48	1.527(3)	C62-C63	1.532(2)
C44-C45	1.534(3)	C62-H62	1.00
C44-H44	1.00	C63-C64	1.520(3)
C45-C46	1.561(3)	C63-H63A	0.99
C45-H45	1.00	C63-H63B	0.99
C46-C47	1.536(3)	C64-H64	1.00
C46-H46	1.00	C1A-C2A	1.544(6)
C47-C48	1.513(3)	C1A-H1A1	0.98
C47-H47A	0.99	C1A-H1A2	0.98
C47-H47B	0.99	C1A-H1A3	0.98
C48-H48	1.00	C2A-C3A	1.526(6)
O7-C49	1.4342(19)	C2A-H2A1	0.99
O7-H7O	0.79(3)	C2A-H2A2	0.99
O8-C57	1.4332(19)	C3A-C4A	1.556(6)
O8-H8O	0.82(3)	C3A-H3A1	0.99
C49-C61	1.536(2)	C3A-H3A2	0.99
C49-C50	1.545(2)	C4A-C5A	1.566(6)
C49-C57	1.601(2)	C4A-H4A1	0.99
C50-C51	1.513(2)	C4A-H4A2	0.99
C50-H50A	0.99	C5A-H5A1	0.98
C50-H50B	0.99	C5A-H5A2	0.98
C51-C56	1.398(2)	C5A-H5A3	0.98
C51-C52	1.402(3)	Cl1-C1B	1.780(7)
C52-C53	1.393(3)	Cl2-C1B	1.779(7)
C52-H52	0.95	C1B-H1BA	0.99
C53-C54	1.400(3)	C1B-H1BB	0.99

C1-O1-H1O	107(2)	C9-O2-H2O	107.7(18)

O1-C1-C13	113.35(14)	C16-C11-H11	122.7
O1-C1-C2	107.90(13)	C10-C11-H11	122.7
C13-C1-C2	113.04(14)	C16-C12-C11	60.11(12)
O1-C1-C9	113.22(13)	C16-C12-C13	108.48(15)
C13-C1-C9	102.63(13)	C11-C12-C13	104.94(15)
C2-C1-C9	106.54(13)	C16-C12-H12	122.3
C3-C2-C1	105.71(14)	C11-C12-H12	122.3
C3-C2-H2A	110.6	C13-C12-H12	122.3
C1-C2-H2A	110.6	C12-C13-C1	111.30(14)
C3-C2-H2B	110.6	C12-C13-C14	96.90(14)
C1-C2-H2B	110.6	C1-C13-C14	103.41(13)
H2A-C2-H2B	108.7	C12-C13-H13	114.5
C8-C3-C4	120.24(17)	C1-C13-H13	114.5
C8-C3-C2	111.71(16)	C14-C13-H13	114.5
C4-C3-C2	128.01(17)	C15-C14-C13	104.90(15)
C5-C4-C3	118.86(19)	C15-C14-C10	104.63(15)
C5-C4-H4	120.6	C13-C14-C10	94.16(13)
C3-C4-H4	120.6	C15-C14-H14	116.7
C4-C5-C6	120.83(19)	C13-C14-H14	116.7
C4-C5-H5	119.6	C10-C14-H14	116.7
C6-C5-H5	119.6	C16-C15-C14	97.36(14)
C5-C6-C7	120.50(18)	C16-C15-H15A	112.3
C5-C6-H6	119.8	C14-C15-H15A	112.3
C7-C6-H6	119.8	C16-C15-H15B	112.3
C8-C7-C6	118.72(18)	C14-C15-H15B	112.3
C8-C7-H7	120.6	H15A-C15-H15B	109.9
C6-C7-H7	120.6	C15-C16-C12	107.30(16)
C7-C8-C3	120.83(17)	C15-C16-C11	107.25(16)
C7-C8-C9	127.06(17)	C12-C16-C11	60.07(12)
C3-C8-C9	112.10(15)	C15-C16-H16	122.1
O2-C9-C8	112.19(13)	C12-C16-H16	122.1
O2-C9-C10	109.54(14)	C11-C16-H16	122.1
C8-C9-C10	113.90(14)	C17-O3-H3O	109.6(17)
O2-C9-C1	114.05(13)	C25-O4-H4O	107.6(17)
C8-C9-C1	103.85(13)	O3-C17-C29	113.71(13)
C10-C9-C1	102.96(13)	O3-C17-C18	107.73(13)
C11-C10-C9	109.72(14)	C29-C17-C18	113.05(13)
C11-C10-C14	97.09(14)	O3-C17-C25	113.08(13)
C9-C10-C14	104.05(14)	C29-C17-C25	102.64(12)
C11-C10-H10	114.7	C18-C17-C25	106.45(12)
C9-C10-H10	114.7	C19-C18-C17	105.72(13)
C14-C10-H10	114.7	C19-C18-H18A	110.6
C12-C11-C16	59.83(12)	C17-C18-H18A	110.6
C12-C11-C10	103.97(15)	C19-C18-H18B	110.6
C16-C11-C10	108.24(15)	C17-C18-H18B	110.6
C12-C11-H11	122.7	H18A-C18-H18B	108.7

C24-C19-C20	119.84(16)	C17-C29-H29	114.6
C24-C19-C18	111.67(14)	C30-C29-H29	114.6
C20-C19-C18	128.48(16)	C31-C30-C26	104.83(14)
C21-C20-C19	119.30(17)	C31-C30-C29	105.29(14)
C21-C20-H20	120.3	C26-C30-C29	94.52(12)
C19-C20-H20	120.3	C31-C30-H30	116.5
C20-C21-C22	120.78(17)	C26-C30-H30	116.5
C20-C21-H21	119.6	C29-C30-H30	116.5
C22-C21-H21	119.6	C32-C31-C30	97.08(13)
C21-C22-C23	120.25(17)	C32-C31-H31A	112.3
C21-C22-H22	119.9	C30-C31-H31A	112.3
C23-C22-H22	119.9	C32-C31-H31B	112.3
C22-C23-C24	118.80(17)	C30-C31-H31B	112.3
C22-C23-H23	120.6	H31A-C31-H31B	109.9
C24-C23-H23	120.6	C31-C32-C27	107.36(14)
C19-C24-C23	121.01(16)	C31-C32-C28	107.29(14)
C19-C24-C25	112.06(14)	C27-C32-C28	60.11(11)
C23-C24-C25	126.91(16)	C31-C32-H32	122.1
O4-C25-C24	111.86(13)	C27-C32-H32	122.1
O4-C25-C26	110.10(13)	C28-C32-H32	122.1
C24-C25-C26	112.90(13)	C33-O5-H5O	108.6(18)
O4-C25-C17	114.33(12)	C41-O6-H6O	106.7(19)
C24-C25-C17	104.08(13)	O5-C33-C45	114.17(15)
C26-C25-C17	103.21(12)	O5-C33-C34	107.82(13)
C27-C26-C25	110.83(13)	C45-C33-C34	112.59(14)
C27-C26-C30	97.09(13)	O5-C33-C41	113.08(13)
C25-C26-C30	103.29(13)	C45-C33-C41	102.65(13)
C27-C26-H26	114.6	C34-C33-C41	106.29(14)
C25-C26-H26	114.6	C35-C34-C33	105.79(14)
C30-C26-H26	114.6	C35-C34-H34A	110.6
C32-C27-C28	60.03(11)	C33-C34-H34A	110.6
C32-C27-C26	107.85(14)	C35-C34-H34B	110.6
C28-C27-C26	104.22(14)	C33-C34-H34B	110.6
C32-C27-H27	122.7	H34A-C34-H34B	108.7
C28-C27-H27	122.7	C36-C35-C40	119.90(18)
C26-C27-H27	122.7	C36-C35-C34	128.68(17)
C32-C28-C27	59.86(11)	C40-C35-C34	111.30(17)
C32-C28-C29	108.24(14)	C35-C36-C37	118.9(2)
C27-C28-C29	104.53(13)	C35-C36-H36	120.6
C32-C28-H28	122.5	C37-C36-H36	120.6
C27-C28-H28	122.5	C38-C37-C36	120.9(2)
C29-C28-H28	122.5	C38-C37-H37	119.5
C28-C29-C17	111.00(13)	C36-C37-H37	119.5
C28-C29-C30	96.85(13)	C39-C38-C37	120.41(19)
C17-C29-C30	103.30(13)	C39-C38-H38	119.8
C28-C29-H29	114.6	C37-C38-H38	119.8

C38-C39-C40	118.89(19)	C46-C47-H47B	112.3
C38-C39-H39	120.6	H47A-C47-H47B	109.9
C40-C39-H39	120.6	C47-C48-C43	107.1(2)
C35-C40-C39	121.00(19)	C47-C48-C44	107.60(17)
C35-C40-C41	112.35(16)	C43-C48-C44	60.38(13)
C39-C40-C41	126.60(18)	C47-C48-H48	122.0
O6-C41-C40	112.26(15)	C43-C48-H48	122.0
O6-C41-C42	109.39(15)	C44-C48-H48	122.0
C40-C41-C42	113.63(16)	C49-O7-H7O	107(2)
O6-C41-C33	114.04(14)	C57-O8-H8O	110.1(19)
C40-C41-C33	104.13(14)	O7-C49-C61	113.13(13)
C42-C41-C33	103.04(14)	O7-C49-C50	108.52(13)
C43-C42-C41	110.00(16)	C61-C49-C50	112.63(13)
C43-C42-C46	96.99(16)	O7-C49-C57	112.48(13)
C41-C42-C46	103.91(14)	C61-C49-C57	102.90(12)
C43-C42-H42	114.7	C50-C49-C57	106.98(13)
C41-C42-H42	114.7	C51-C50-C49	105.44(13)
C46-C42-H42	114.7	C51-C50-H50A	110.7
C48-C43-C42	108.11(18)	C49-C50-H50A	110.7
C48-C43-C44	59.92(13)	C51-C50-H50B	110.7
C42-C43-C44	104.45(16)	C49-C50-H50B	110.7
C48-C43-H43	122.6	H50A-C50-H50B	108.8
C42-C43-H43	122.6	C56-C51-C52	119.96(16)
C44-C43-H43	122.6	C56-C51-C50	111.81(15)
C48-C44-C45	107.77(17)	C52-C51-C50	128.22(16)
C48-C44-C43	59.69(13)	C53-C52-C51	119.27(17)
C45-C44-C43	104.07(17)	C53-C52-H52	120.4
C48-C44-H44	122.8	C51-C52-H52	120.4
C45-C44-H44	122.8	C52-C53-C54	120.68(18)
C43-C44-H44	122.8	C52-C53-H53	119.7
C44-C45-C33	111.43(14)	C54-C53-H53	119.7
C44-C45-C46	97.23(15)	C55-C54-C53	120.37(17)
C33-C45-C46	103.08(15)	C55-C54-H54	119.8
C44-C45-H45	114.4	C53-C54-H54	119.8
C33-C45-H45	114.4	C54-C55-C56	118.81(17)
C46-C45-H45	114.4	C54-C55-H55	120.6
C47-C46-C42	104.57(16)	C56-C55-H55	120.6
C47-C46-C45	104.91(17)	C51-C56-C55	120.90(16)
C42-C46-C45	94.43(14)	C51-C56-C57	112.01(14)
C47-C46-H46	116.7	C55-C56-C57	127.08(15)
C42-C46-H46	116.7	O8-C57-C56	111.60(13)
C45-C46-H46	116.7	O8-C57-C58	109.94(13)
C48-C47-C46	97.54(16)	C56-C57-C58	113.84(13)
C48-C47-H47A	112.3	O8-C57-C49	114.49(13)
C46-C47-H47A	112.3	C56-C57-C49	103.62(13)
C48-C47-H47B	112.3	C58-C57-C49	103.02(12)

C59-C58-C57	111.23(13)	C60-C64-H64	122.0
C59-C58-C62	96.91(13)	C63-C64-H64	122.0
C57-C58-C62	102.72(13)	C59-C64-H64	122.0
C59-C58-H58	114.7	C2A-C1A-H1A1	109.5
C57-C58-H58	114.7	C2A-C1A-H1A2	109.5
C62-C58-H58	114.7	H1A1-C1A-H1A2	109.5
C64-C59-C60	59.46(11)	C2A-C1A-H1A3	109.5
C64-C59-C58	107.90(14)	H1A1-C1A-H1A3	109.5
C60-C59-C58	104.57(13)	H1A2-C1A-H1A3	109.5
C64-C59-H59	122.7	C3A-C2A-C1A	108.4(5)
C60-C59-H59	122.7	C3A-C2A-H2A1	110.0
C58-C59-H59	122.7	C1A-C2A-H2A1	110.0
C64-C60-C61	108.46(14)	C3A-C2A-H2A2	110.0
C64-C60-C59	60.07(11)	C1A-C2A-H2A2	110.0
C61-C60-C59	104.20(14)	H2A1-C2A-H2A2	108.4
C64-C60-H60	122.5	C2A-C3A-C4A	110.6(4)
C61-C60-H60	122.5	C2A-C3A-H3A1	109.5
C59-C60-H60	122.5	C4A-C3A-H3A1	109.5
C60-C61-C49	110.14(13)	C2A-C3A-H3A2	109.5
C60-C61-C62	97.08(13)	C4A-C3A-H3A2	109.5
C49-C61-C62	104.10(13)	H3A1-C3A-H3A2	108.1
C60-C61-H61	114.6	C3A-C4A-C5A	107.0(5)
C49-C61-H61	114.6	C3A-C4A-H4A1	110.3
C62-C61-H61	114.6	C5A-C4A-H4A1	110.3
C63-C62-C58	104.93(13)	C3A-C4A-H4A2	110.3
C63-C62-C61	104.78(14)	C5A-C4A-H4A2	110.3
C58-C62-C61	94.32(12)	H4A1-C4A-H4A2	108.6
C63-C62-H62	116.6	C4A-C5A-H5A1	109.5
C58-C62-H62	116.6	C4A-C5A-H5A2	109.5
C61-C62-H62	116.6	H5A1-C5A-H5A2	109.5
C64-C63-C62	97.30(13)	C4A-C5A-H5A3	109.5
C64-C63-H63A	112.3	H5A1-C5A-H5A3	109.5
C62-C63-H63A	112.3	H5A2-C5A-H5A3	109.5
C64-C63-H63B	112.3	Cl2-C1B-Cl1	112.3(4)
C62-C63-H63B	112.3	Cl2-C1B-H1BA	109.1
H63A-C63-H63B	109.9	Cl1-C1B-H1BA	109.1
C60-C64-C63	107.23(14)	Cl2-C1B-H1BB	109.1
C60-C64-C59	60.47(11)	Cl1-C1B-H1BB	109.1
C63-C64-C59	107.42(15)	H1BA-C1B-H1BB	107.9

Table 5.26. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5.4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O1	24(1)	14(1)	23(1)	-2(1)	1(1)	-7(1)
O2	19(1)	19(1)	25(1)	-12(1)	-1(1)	-3(1)
C1	22(1)	13(1)	18(1)	-4(1)	2(1)	-5(1)
C2	21(1)	18(1)	24(1)	-4(1)	3(1)	-4(1)
C3	27(1)	12(1)	22(1)	-4(1)	-1(1)	-5(1)
C4	32(1)	14(1)	34(1)	-2(1)	-9(1)	-4(1)
C5	52(1)	17(1)	29(1)	4(1)	-18(1)	-8(1)
C6	54(1)	24(1)	19(1)	1(1)	-5(1)	-13(1)
C7	35(1)	21(1)	20(1)	-4(1)	3(1)	-11(1)
C8	27(1)	13(1)	19(1)	-4(1)	1(1)	-8(1)
C9	20(1)	14(1)	18(1)	-5(1)	2(1)	-6(1)
C10	24(1)	21(1)	19(1)	-7(1)	3(1)	-11(1)
C11	24(1)	23(1)	30(1)	-12(1)	-4(1)	-6(1)
C12	34(1)	20(1)	21(1)	-5(1)	-5(1)	-9(1)
C13	27(1)	17(1)	18(1)	-7(1)	3(1)	-7(1)
C14	29(1)	15(1)	22(1)	-5(1)	1(1)	-7(1)
C15	37(1)	21(1)	28(1)	-10(1)	-1(1)	-12(1)
C16	34(1)	26(1)	27(1)	-11(1)	-7(1)	-11(1)
O3	13(1)	14(1)	24(1)	-2(1)	-3(1)	-4(1)
O4	21(1)	14(1)	22(1)	-3(1)	-7(1)	-3(1)
C17	13(1)	12(1)	20(1)	-2(1)	-2(1)	-3(1)
C18	17(1)	14(1)	22(1)	0(1)	-5(1)	-2(1)
C19	15(1)	13(1)	27(1)	-4(1)	-4(1)	-4(1)
C20	18(1)	12(1)	40(1)	-2(1)	-6(1)	-3(1)
C21	17(1)	16(1)	47(1)	-10(1)	-1(1)	-3(1)
C22	21(1)	22(1)	37(1)	-12(1)	7(1)	-7(1)
C23	22(1)	17(1)	26(1)	-5(1)	1(1)	-6(1)
C24	15(1)	13(1)	25(1)	-5(1)	-2(1)	-4(1)
C25	13(1)	12(1)	18(1)	-2(1)	-3(1)	-2(1)
C26	19(1)	12(1)	23(1)	-2(1)	-3(1)	-4(1)
C27	21(1)	12(1)	25(1)	-3(1)	-6(1)	-1(1)
C28	19(1)	14(1)	25(1)	-6(1)	-4(1)	-2(1)
C29	18(1)	14(1)	19(1)	-3(1)	-4(1)	-4(1)
C30	17(1)	15(1)	26(1)	-4(1)	-6(1)	-4(1)
C31	26(1)	16(1)	32(1)	-7(1)	-8(1)	-7(1)
C32	26(1)	14(1)	28(1)	-6(1)	-6(1)	-3(1)
O5	23(1)	20(1)	14(1)	-2(1)	-2(1)	1(1)
O6	32(1)	15(1)	21(1)	2(1)	8(1)	-2(1)
C33	28(1)	16(1)	14(1)	-1(1)	-1(1)	-3(1)
C34	28(1)	15(1)	19(1)	-1(1)	-5(1)	-4(1)
C35	35(1)	21(1)	14(1)	2(1)	-7(1)	-8(1)

C36	42(1)	29(1)	27(1)	5(1)	-18(1)	-9(1)
C37	48(1)	44(1)	35(1)	5(1)	-26(1)	-16(1)
C38	60(2)	38(1)	24(1)	-1(1)	-16(1)	-25(1)
C39	51(1)	26(1)	16(1)	-4(1)	-3(1)	-16(1)
C40	40(1)	22(1)	11(1)	0(1)	-2(1)	-10(1)
C41	34(1)	14(1)	15(1)	-1(1)	3(1)	-5(1)
C42	48(1)	19(1)	20(1)	-6(1)	11(1)	-10(1)
C43	44(1)	19(1)	28(1)	0(1)	19(1)	-1(1)
C44	30(1)	23(1)	24(1)	1(1)	7(1)	0(1)
C45	30(1)	17(1)	17(1)	0(1)	1(1)	-5(1)
C46	43(1)	23(1)	16(1)	-1(1)	4(1)	-12(1)
C47	55(1)	28(1)	20(1)	-4(1)	14(1)	-16(1)
C48	44(1)	23(1)	32(1)	-2(1)	19(1)	-4(1)
O7	20(1)	18(1)	15(1)	-4(1)	-1(1)	-1(1)
O8	13(1)	22(1)	18(1)	-1(1)	-1(1)	-3(1)
C49	15(1)	16(1)	15(1)	-4(1)	-2(1)	-2(1)
C50	19(1)	19(1)	18(1)	-3(1)	-6(1)	-4(1)
C51	17(1)	20(1)	19(1)	-5(1)	-2(1)	-3(1)
C52	24(1)	22(1)	27(1)	-4(1)	-9(1)	0(1)
C53	30(1)	18(1)	35(1)	-4(1)	-8(1)	2(1)
C54	33(1)	18(1)	39(1)	-9(1)	-8(1)	-4(1)
C55	24(1)	21(1)	28(1)	-6(1)	-7(1)	-4(1)
C56	15(1)	18(1)	17(1)	-3(1)	-1(1)	-3(1)
C57	14(1)	17(1)	16(1)	-4(1)	-1(1)	-3(1)
C58	16(1)	21(1)	15(1)	-5(1)	-2(1)	-5(1)
C59	19(1)	23(1)	13(1)	-1(1)	-3(1)	-6(1)
C60	19(1)	19(1)	16(1)	-3(1)	0(1)	-5(1)
C61	15(1)	19(1)	15(1)	-4(1)	-1(1)	-5(1)
C62	15(1)	21(1)	17(1)	-5(1)	0(1)	-5(1)
C63	21(1)	28(1)	17(1)	-6(1)	3(1)	-9(1)
C64	24(1)	23(1)	15(1)	0(1)	-1(1)	-7(1)
C1A	56(4)	64(4)	52(4)	-19(3)	7(4)	-4(4)
C2A	75(5)	43(3)	40(3)	-12(2)	11(3)	-25(3)
C3A	51(4)	65(3)	33(2)	-4(2)	-4(3)	-27(4)
C4A	46(3)	41(3)	67(3)	-23(3)	-30(3)	10(2)
C5A	100(5)	58(4)	25(3)	-5(2)	-10(3)	-10(4)
Cl1	53(1)	37(1)	36(1)	-3(1)	-10(1)	-1(1)
Cl2	42(1)	37(1)	34(1)	-11(1)	-2(1)	-4(1)

Table 5.27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5.4c**.

	x	y	z	U(eq)
H2A	5020	7145	2787	26
H2B	5249	8364	2926	26
H4	4293	8842	1609	31
H5	5028	9162	427	38
H6	7033	8598	35	38
H7	8342	7692	823	30
H10	9051	8252	2046	25
H11	9958	6536	2926	29
H12	8382	6377	4022	29
H13	6562	8001	3799	24
H14	7133	9329	2676	26
H15A	9026	9616	3023	33
H15B	8047	9522	3709	33
H16	9799	7827	3877	33
H18A	5814	6165	1159	21
H18B	5109	5391	855	21
H20	3277	7079	1541	28
H21	1900	7015	2551	32
H22	2231	5558	3489	32
H23	3963	4143	3427	26
H26	4991	2386	2616	21
H27	7255	1523	2453	23
H28	8104	2264	1186	23
H29	6345	3566	608	20
H30	4426	3343	1430	22
H31A	4863	1145	1615	28
H31B	5391	1602	826	28
H32	7132	439	1450	26
H34A	9536	517	4473	25
H34B	10018	870	3669	25
H36	12052	627	4406	38
H37	13155	1942	4610	48
H38	12309	3891	4635	45
H39	10336	4563	4472	36
H42	8050	3984	5157	36
H43	6289	4585	4440	42
H44	5878	2680	4125	34
H45	7396	969	4667	27
H46	8460	1765	5452	33
H47A	6329	1618	5916	43

H47B	6585	2804	6103	43
H48	4961	3347	5315	44
H50A	12848	2913	2504	22
H50B	11772	2877	3133	22
H52	13056	462	3057	29
H53	12589	-1201	2775	34
H54	11175	-1040	2049	35
H55	10217	798	1586	28
H58	10764	2858	733	20
H59	9517	4948	799	22
H60	10688	6053	1381	21
H61	12596	4607	1677	19
H62	12782	2804	1092	21
H63A	13180	4616	280	27
H63B	12461	3931	-88	27
H64	11189	5951	68	25
H1A1	755	8347	892	89
H1A2	2085	8264	508	89
H1A3	1109	7936	145	89
H2A1	1158	10244	378	62
H2A2	1424	9823	-369	62
H3A1	-814	9972	516	57
H3A2	-562	9443	-196	57
H4A1	-247	11301	-833	59
H4A2	-475	11834	-120	59
H5A1	-2228	10932	-627	92
H5A2	-2289	12278	-601	92
H5A3	-2459	11400	103	92
H1BA	5287	-1111	4644	45
H1BB	6360	-443	4582	45
H1O	7330(30)	5560(30)	3358(15)	53(8)
H2O	8040(20)	5690(20)	1952(14)	44(7)
H3O	7890(20)	4130(20)	1603(13)	33(7)
H4O	6530(20)	4460(20)	2853(12)	24(6)
H5O	7660(30)	2690(30)	3284(14)	49(8)
H6O	9140(20)	4180(20)	3385(14)	42(7)
H7O	9970(20)	4860(20)	2390(15)	45(8)
H8O	9090(20)	2900(20)	2403(15)	47(8)

Table 5.28. Torsion angles [°] for **5.4c**.

O1-C1-C2-C3	-120.24(14)	C16-C12-C13-C1	132.90(15)
C13-C1-C2-C3	113.61(15)	C11-C12-C13-C1	69.94(17)
C9-C1-C2-C3	1.64(17)	C16-C12-C13-C14	25.57(17)
C1-C2-C3-C8	0.15(18)	C11-C12-C13-C14	-37.39(15)
C1-C2-C3-C4	177.96(16)	O1-C1-C13-C12	55.76(18)
C8-C3-C4-C5	1.5(3)	C2-C1-C13-C12	178.95(14)
C2-C3-C4-C5	-176.11(17)	C9-C1-C13-C12	-66.70(17)
C3-C4-C5-C6	-1.0(3)	O1-C1-C13-C14	158.79(14)
C4-C5-C6-C7	0.0(3)	C2-C1-C13-C14	-78.03(17)
C5-C6-C7-C8	0.5(3)	C9-C1-C13-C14	36.33(16)
C6-C7-C8-C3	0.0(3)	C12-C13-C14-C15	-46.59(16)
C6-C7-C8-C9	178.85(16)	C1-C13-C14-C15	-160.48(14)
C4-C3-C8-C7	-1.0(2)	C12-C13-C14-C10	59.74(14)
C2-C3-C8-C7	176.96(15)	C1-C13-C14-C10	-54.14(16)
C4-C3-C8-C9	179.96(15)	C11-C10-C14-C15	46.48(16)
C2-C3-C8-C9	-2.04(19)	C9-C10-C14-C15	158.91(14)
C7-C8-C9-O2	-52.4(2)	C11-C10-C14-C13	-60.10(14)
C3-C8-C9-O2	126.56(15)	C9-C10-C14-C13	52.33(16)
C7-C8-C9-C10	72.8(2)	C13-C14-C15-C16	48.95(17)
C3-C8-C9-C10	-108.28(16)	C10-C14-C15-C16	-49.50(17)
C7-C8-C9-C1	-175.99(16)	C14-C15-C16-C12	-31.05(18)
C3-C8-C9-C1	2.93(17)	C14-C15-C16-C11	32.17(18)
O1-C1-C9-O2	-6.7(2)	C11-C12-C16-C15	100.31(17)
C13-C1-C9-O2	115.89(15)	C13-C12-C16-C15	3.34(19)
C2-C1-C9-O2	-125.10(15)	C13-C12-C16-C11	-96.97(16)
O1-C1-C9-C8	115.75(15)	C12-C11-C16-C15	-100.40(17)
C13-C1-C9-C8	-121.70(14)	C10-C11-C16-C15	-4.5(2)
C2-C1-C9-C8	-2.69(16)	C10-C11-C16-C12	95.88(16)
O1-C1-C9-C10	-125.25(15)	O3-C17-C18-C19	-122.70(14)
C13-C1-C9-C10	-2.70(16)	C29-C17-C18-C19	110.80(15)
C2-C1-C9-C10	116.31(14)	C25-C17-C18-C19	-1.13(16)
O2-C9-C10-C11	-50.41(17)	C17-C18-C19-C24	1.03(18)
C8-C9-C10-C11	-176.97(14)	C17-C18-C19-C20	-178.30(16)
C1-C9-C10-C11	71.28(16)	C24-C19-C20-C21	-0.8(3)
O2-C9-C10-C14	-153.40(14)	C18-C19-C20-C21	178.49(17)
C8-C9-C10-C14	80.04(17)	C19-C20-C21-C22	0.6(3)
C1-C9-C10-C14	-31.71(16)	C20-C21-C22-C23	0.2(3)
C9-C10-C11-C12	-70.14(16)	C21-C22-C23-C24	-0.8(3)
C14-C10-C11-C12	37.59(15)	C20-C19-C24-C23	0.2(2)
C9-C10-C11-C16	-132.53(15)	C18-C19-C24-C23	-179.17(15)
C14-C10-C11-C16	-24.81(17)	C20-C19-C24-C25	178.91(15)
C10-C11-C12-C16	-103.20(16)	C18-C19-C24-C25	-0.49(19)
C16-C11-C12-C13	103.00(16)	C22-C23-C24-C19	0.6(3)
C10-C11-C12-C13	-0.20(17)	C22-C23-C24-C25	-177.92(16)

C19-C24-C25-O4	123.69(15)	C26-C30-C31-C32	-49.70(16)
C23-C24-C25-O4	-57.7(2)	C29-C30-C31-C32	49.33(16)
C19-C24-C25-C26	-111.46(16)	C30-C31-C32-C27	31.80(17)
C23-C24-C25-C26	67.1(2)	C30-C31-C32-C28	-31.49(17)
C19-C24-C25-C17	-0.25(17)	C28-C27-C32-C31	-100.34(16)
C23-C24-C25-C17	178.33(16)	C26-C27-C32-C31	-3.90(19)
O3-C17-C25-O4	-3.37(18)	C26-C27-C32-C28	96.44(15)
C29-C17-C25-O4	119.55(14)	C27-C28-C32-C31	100.45(16)
C18-C17-C25-O4	-121.47(14)	C29-C28-C32-C31	3.90(19)
O3-C17-C25-C24	118.96(14)	C29-C28-C32-C27	-96.55(15)
C29-C17-C25-C24	-118.12(13)	O5-C33-C34-C35	120.55(14)
C18-C17-C25-C24	0.86(16)	C45-C33-C34-C35	-112.62(16)
O3-C17-C25-C26	-122.94(14)	C41-C33-C34-C35	-0.98(17)
C29-C17-C25-C26	-0.02(15)	C33-C34-C35-C36	-177.27(18)
C18-C17-C25-C26	118.96(14)	C33-C34-C35-C40	-1.36(19)
O4-C25-C26-C27	-53.49(18)	C40-C35-C36-C37	-1.4(3)
C24-C25-C26-C27	-179.29(14)	C34-C35-C36-C37	174.20(19)
C17-C25-C26-C27	68.96(16)	C35-C36-C37-C38	0.1(3)
O4-C25-C26-C30	-156.53(13)	C36-C37-C38-C39	0.7(3)
C24-C25-C26-C30	77.67(16)	C37-C38-C39-C40	-0.2(3)
C17-C25-C26-C30	-34.08(15)	C36-C35-C40-C39	1.9(3)
C25-C26-C27-C32	-132.62(14)	C34-C35-C40-C39	-174.38(15)
C30-C26-C27-C32	-25.45(16)	C36-C35-C40-C41	179.69(16)
C25-C26-C27-C28	-70.00(16)	C34-C35-C40-C41	3.4(2)
C30-C26-C27-C28	37.17(15)	C38-C39-C40-C35	-1.1(3)
C26-C27-C28-C32	-102.65(15)	C38-C39-C40-C41	-178.55(17)
C32-C27-C28-C29	102.91(15)	C35-C40-C41-O6	-127.64(16)
C26-C27-C28-C29	0.26(16)	C39-C40-C41-O6	50.0(2)
C32-C28-C29-C17	132.19(14)	C35-C40-C41-C42	107.56(17)
C27-C28-C29-C17	69.62(16)	C39-C40-C41-C42	-74.8(2)
C32-C28-C29-C30	25.08(16)	C35-C40-C41-C33	-3.79(18)
C27-C28-C29-C30	-37.49(15)	C39-C40-C41-C33	173.81(16)
O3-C17-C29-C28	53.70(18)	O5-C33-C41-O6	7.3(2)
C18-C17-C29-C28	176.96(13)	C45-C33-C41-O6	-116.15(16)
C25-C17-C29-C28	-68.79(15)	C34-C33-C41-O6	125.45(15)
O3-C17-C29-C30	156.53(13)	O5-C33-C41-C40	-115.35(15)
C18-C17-C29-C30	-80.22(16)	C45-C33-C41-C40	121.16(14)
C25-C17-C29-C30	34.03(15)	C34-C33-C41-C40	2.76(16)
C27-C26-C30-C31	47.22(15)	O5-C33-C41-C42	125.79(16)
C25-C26-C30-C31	160.64(13)	C45-C33-C41-C42	2.30(18)
C27-C26-C30-C29	-59.91(13)	C34-C33-C41-C42	-116.10(16)
C25-C26-C30-C29	53.51(14)	O6-C41-C42-C43	50.8(2)
C28-C29-C30-C31	-46.75(16)	C40-C41-C42-C43	177.17(15)
C17-C29-C30-C31	-160.28(13)	C33-C41-C42-C43	-70.81(18)
C28-C29-C30-C26	59.97(13)	O6-C41-C42-C46	153.77(16)
C17-C29-C30-C26	-53.55(14)	C40-C41-C42-C46	-79.91(19)

C33-C41-C42-C46	32.11(19)	C52-C51-C56-C55	1.2(3)
C41-C42-C43-C48	132.66(16)	C50-C51-C56-C55	-177.69(15)
C46-C42-C43-C48	25.06(19)	C52-C51-C56-C57	-179.72(15)
C41-C42-C43-C44	70.06(18)	C50-C51-C56-C57	1.4(2)
C46-C42-C43-C44	-37.54(17)	C54-C55-C56-C51	-0.3(3)
C42-C43-C44-C48	102.81(18)	C54-C55-C56-C57	-179.27(17)
C48-C43-C44-C45	-102.58(18)	C51-C56-C57-O8	-122.58(15)
C42-C43-C44-C45	0.22(18)	C55-C56-C57-O8	56.5(2)
C48-C44-C45-C33	-132.19(16)	C51-C56-C57-C58	112.25(16)
C43-C44-C45-C33	-69.97(18)	C55-C56-C57-C58	-68.7(2)
C48-C44-C45-C46	-25.04(18)	C51-C56-C57-C49	1.11(17)
C43-C44-C45-C46	37.19(16)	C55-C56-C57-C49	-179.85(16)
O5-C33-C45-C44	-55.3(2)	O7-C49-C57-O8	-0.40(19)
C34-C33-C45-C44	-178.70(15)	C61-C49-C57-O8	-122.47(14)
C41-C33-C45-C44	67.42(18)	C50-C49-C57-O8	118.67(15)
O5-C33-C45-C46	-158.63(14)	O7-C49-C57-C56	-122.18(14)
C34-C33-C45-C46	78.00(17)	C61-C49-C57-C56	115.75(13)
C41-C33-C45-C46	-35.88(17)	C50-C49-C57-C56	-3.11(16)
C43-C42-C46-C47	-46.69(18)	O7-C49-C57-C58	118.94(14)
C41-C42-C46-C47	-159.35(17)	C61-C49-C57-C58	-3.13(15)
C43-C42-C46-C45	59.98(16)	C50-C49-C57-C58	-121.99(14)
C41-C42-C46-C45	-52.68(18)	O8-C57-C58-C59	56.32(17)
C44-C45-C46-C47	46.38(17)	C56-C57-C58-C59	-177.63(13)
C33-C45-C46-C47	160.43(15)	C49-C57-C58-C59	-66.13(16)
C44-C45-C46-C42	-59.99(16)	O8-C57-C58-C62	159.03(13)
C33-C45-C46-C42	54.06(17)	C56-C57-C58-C62	-74.92(16)
C42-C46-C47-C48	49.75(19)	C49-C57-C58-C62	36.58(15)
C45-C46-C47-C48	-48.99(18)	C57-C58-C59-C64	132.00(14)
C46-C47-C48-C43	-32.2(2)	C62-C58-C59-C64	25.43(15)
C46-C47-C48-C44	31.4(2)	C57-C58-C59-C60	69.88(16)
C42-C43-C48-C47	4.3(2)	C62-C58-C59-C60	-36.68(14)
C44-C43-C48-C47	100.87(18)	C58-C59-C60-C64	102.43(14)
C42-C43-C48-C44	-96.54(17)	C64-C59-C60-C61	-103.37(14)
C45-C44-C48-C47	-3.9(2)	C58-C59-C60-C61	-0.94(16)
C43-C44-C48-C47	-100.1(2)	C64-C60-C61-C49	-132.44(14)
C45-C44-C48-C43	96.22(18)	C59-C60-C61-C49	-69.70(16)
O7-C49-C50-C51	125.50(14)	C64-C60-C61-C62	-24.56(16)
C61-C49-C50-C51	-108.44(15)	C59-C60-C61-C62	38.18(14)
C57-C49-C50-C51	3.90(16)	O7-C49-C61-C60	-49.96(18)
C49-C50-C51-C56	-3.40(19)	C50-C49-C61-C60	-173.49(13)
C49-C50-C51-C52	177.86(17)	C57-C49-C61-C60	71.68(15)
C56-C51-C52-C53	-1.3(3)	O7-C49-C61-C62	-153.11(13)
C50-C51-C52-C53	177.38(17)	C50-C49-C61-C62	83.36(15)
C51-C52-C53-C54	0.5(3)	C57-C49-C61-C62	-31.47(15)
C52-C53-C54-C55	0.4(3)	C59-C58-C62-C63	-47.04(15)
C53-C54-C55-C56	-0.5(3)	C57-C58-C62-C63	-160.70(13)

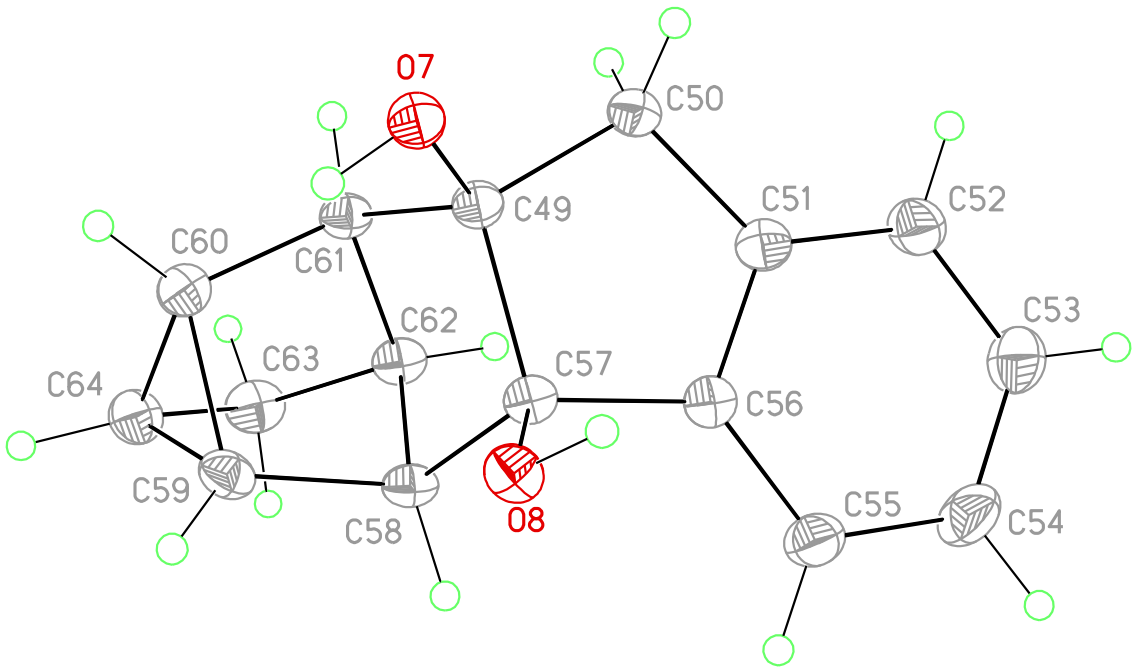
C59-C58-C62-C61	59.52(13)	C59-C60-C64-C63	-100.64(15)
C57-C58-C62-C61	-54.15(14)	C61-C60-C64-C59	96.10(15)
C60-C61-C62-C63	46.26(15)	C62-C63-C64-C60	32.09(16)
C49-C61-C62-C63	159.15(13)	C62-C63-C64-C59	-31.58(16)
C60-C61-C62-C58	-60.42(13)	C58-C59-C64-C60	-96.68(14)
C49-C61-C62-C58	52.46(14)	C60-C59-C64-C63	100.31(15)
C58-C62-C63-C64	49.48(15)	C58-C59-C64-C63	3.63(18)
C61-C62-C63-C64	-49.20(15)	C1A-C2A-C3A-C4A	-175.1(6)
C61-C60-C64-C63	-4.54(18)	C2A-C3A-C4A-C5A	-179.0(5)

Table 5.29. Hydrogen bonds for **5.4c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O4-H4O...O1	0.79(2)	2.04(2)	2.8133(19)	167(2)
O6-H6O...O7	0.83(3)	1.95(3)	2.7655(19)	167(3)
O8-H8O...O5	0.82(3)	2.06(3)	2.8686(19)	169(3)
O3-H3O...O8	0.81(3)	1.98(3)	2.7566(19)	161(2)
O5-H5O...O4	0.88(3)	1.95(3)	2.7831(19)	157(3)
O1-H1O...O6	0.86(3)	2.00(3)	2.805(2)	157(3)
O7-H7O...O2	0.79(3)	2.09(3)	2.841(2)	159(3)
O2-H2O...O3	0.84(3)	1.98(3)	2.8134(18)	167(3)
C13-H13...Cl2#1	1.00	2.90	3.820(2)	153.6
C26-H26...Cl1	1.00	2.99	3.791(2)	137.8

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Figure 5.5. View of **5.4c** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **5.4d**-CH_2Cl_2

X-ray Experimental for $3C_{19}H_{16}O_2$ - CH_2Cl_2: Crystals grew as clear, colorless prisms by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.2 x 0.1 x 0.1 mm. The data were collected at -173 ˚C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoK α radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 700 low-temperature device. A total of 1778 frames of data were collected using ω and α-scans with a scan range of 0.6˚ and a counting time of 26 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.[42] The structure was solved by direct methods using SHELXT[30] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[31] Structure analysis was aided by use of the programs PLATON[32] and WinGX.[33] The hydrogen atoms were calculated in idealized positions.

The function, $\Sigma w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.0577*P)^2 + (7.8793*P)]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. Rw(F2) refined to 0.159, with R(F) equal to 0.0641 and a goodness of fit, S, = 1.07. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[10] The data were corrected for secondary extinction effects. The correction takes the form: $Fcorr = kFc/[1 + (1.23(11)x10\text{-}5)* Fc2\ \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[35] All figures were generated using SHELXTL/PC.[36] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.30. Crystal data and structure refinement for **5.4d**.

Empirical formula	C58 H50 Cl2 O6	
Formula weight	913.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	P 32 2 1	
Unit cell dimensions	a = 13.918(4) Å	α= 90°.
	b = 13.918(4) Å	β= 90°.
	c = 39.129(11) Å	γ = 120°.
Volume	6564(4) $Å^3$	
Z	6	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	0.206 mm^{-1}	
F(000)	2880	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Theta range for data collection	2.682 to 24.905°.	
Index ranges	-16<=h<=16, -16<=k<=16, -46<=l<=42	
Reflections collected	89244	
Independent reflections	7646 [R(int) = 0.1784]	
Completeness to theta = 24.905°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7646 / 402 / 612	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1527	
R indices (all data)	R1 = 0.0755, wR2 = 0.1587	
Absolute structure parameter	0.11(12)	
Extinction coefficient	$1.23(11)x10^{-5}$	
Largest diff. peak and hole	0.536 and -0.678 $e.Å^{-3}$	

Table 5.31. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.4d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	6454(4)	1327(4)	7669(1)	15(1)
C2	6468(4)	2400(4)	7756(1)	16(1)
C3	6557(5)	2909(5)	8064(2)	23(1)
C4	6599(5)	3951(5)	8060(2)	27(1)
C5	6589(5)	4473(5)	7760(2)	26(1)
C6	6506(5)	3956(5)	7440(2)	21(1)
C7	6530(5)	4388(5)	7110(2)	28(2)
C8	6476(5)	3784(5)	6822(2)	28(1)
C9	6395(5)	2739(5)	6842(2)	23(1)
C10	6365(4)	2302(5)	7156(2)	18(1)
C11	6338(4)	1242(4)	7259(1)	14(1)
C12	6439(4)	2925(4)	7447(2)	17(1)
C13	5402(4)	292(4)	7788(1)	16(1)
C14	5432(4)	-761(4)	7697(1)	18(1)
C15	4333(5)	-1569(5)	7537(2)	24(1)
C16	5304(4)	-836(5)	7309(2)	20(1)
C17	5209(4)	178(4)	7211(2)	17(1)
C18	4524(4)	153(4)	7523(1)	17(1)
C19	3598(4)	-1050(5)	7557(2)	20(1)
C20	8749(5)	-452(4)	7744(1)	15(1)
C21	7702(4)	-1464(4)	7873(1)	15(1)
C22	7318(5)	-1795(5)	8198(1)	20(1)
C23	6272(5)	-2773(5)	8239(2)	23(1)
C24	5636(5)	-3385(5)	7967(2)	24(1)
C25	6009(5)	-3052(4)	7629(1)	18(1)
C26	5442(5)	-3563(5)	7319(2)	22(1)
C27	5911(5)	-3091(5)	7010(2)	21(1)
C28	6958(5)	-2106(5)	6982(1)	19(1)
C29	7531(4)	-1609(4)	7280(1)	16(1)
C30	8624(4)	-557(4)	7333(1)	14(1)
C31	7057(4)	-2081(4)	7594(1)	15(1)
C32	9803(4)	-488(5)	7806(1)	18(1)
C33	10808(5)	580(5)	7678(2)	20(1)
C34	11523(5)	260(5)	7478(2)	24(1)
C35	10700(5)	484(5)	7292(2)	21(1)
C36	9645(4)	-631(4)	7225(2)	17(1)
C37	9796(5)	-1265(5)	7527(2)	19(1)
C38	11010(5)	-991(5)	7504(2)	28(1)
C39	10558(4)	3632(4)	7683(1)	14(1)
C40	11609(4)	3586(4)	7750(1)	14(1)
C41	12122(5)	3585(4)	8049(2)	21(1)

C42	13088(5)	3507(5)	8031(2)	26(1)
C43	13540(5)	3436(4)	7724(2)	22(1)
C44	13027(4)	3436(4)	7411(2)	20(1)
C45	13374(5)	3363(5)	7076(2)	24(1)
C46	12758(5)	3336(5)	6797(2)	23(1)
C47	11754(5)	3374(4)	6833(1)	19(1)
C48	11421(4)	3470(4)	7150(1)	15(1)
C49	10414(4)	3519(4)	7274(1)	14(1)
C50	12063(4)	3511(4)	7437(1)	17(1)
C51	10657(4)	4759(4)	7753(1)	15(1)
C52	9539(5)	4686(4)	7692(1)	18(1)
C53	9740(5)	5670(5)	7472(1)	21(1)
C54	9389(5)	4573(4)	7302(2)	18(1)
C55	10427(4)	4585(4)	7176(1)	15(1)
C56	11255(5)	5458(4)	7430(1)	18(1)
C57	10982(5)	6390(4)	7427(2)	20(1)
C58	2293(7)	0	6667	39(2)
C59	10000	-3333(6)	8333	34(2)
Cl1	2427(1)	-1203(1)	6634(1)	41(1)
Cl2	8810(1)	-3205(1)	8270(1)	38(1)
O1	7411(3)	1319(3)	7795(1)	19(1)
O2	7172(3)	1120(3)	7088(1)	19(1)
O5	9636(3)	2792(3)	7869(1)	18(1)
O6	9402(3)	2581(3)	7168(1)	18(1)
O3	8848(3)	542(3)	7881(1)	20(1)
O4	8649(3)	369(3)	7169(1)	20(1)

Table 5.32. Bond lengths [Å] and angles [°] for **5.4d**.

C1-O1	1.424(6)	C20-C30	1.619(8)
C1-C2	1.522(7)	C21-C22	1.366(8)
C1-C13	1.526(7)	C21-C31	1.402(8)
C1-C11	1.609(7)	C22-C23	1.420(8)
C2-C3	1.372(8)	C22-H22	0.95
C2-C12	1.423(8)	C23-C24	1.375(9)
C3-C4	1.422(8)	C23-H23	0.95
C3-H3	0.95	C24-C25	1.411(8)
C4-C5	1.381(9)	C24-H24	0.95
C4-H4	0.95	C25-C31	1.414(8)
C5-C6	1.422(9)	C25-C26	1.430(8)
C5-H5	0.95	C26-C27	1.373(8)
C6-C12	1.390(8)	C26-H26	0.95
C6-C7	1.416(9)	C27-C28	1.421(8)
C7-C8	1.386(9)	C27-H27	0.95
C7-H7	0.95	C28-C29	1.387(8)
C8-C9	1.404(9)	C28-H28	0.95
C8-H8	0.95	C29-C31	1.396(8)
C9-C10	1.361(8)	C29-C30	1.508(7)
C9-H9	0.95	C30-O4	1.423(6)
C10-C12	1.406(8)	C30-C36	1.535(7)
C10-C11	1.512(8)	C32-C33	1.530(8)
C11-O2	1.423(6)	C32-C37	1.533(8)
C11-C17	1.540(7)	C32-H32	1.00
C13-C14	1.529(7)	C33-C34	1.498(8)
C13-C18	1.540(7)	C33-C35	1.517(8)
C13-H13	1.00	C33-H33	1.00
C14-C15	1.509(8)	C34-C35	1.514(8)
C14-C16	1.527(8)	C34-C38	1.520(8)
C14-H14	1.00	C34-H34	1.00
C15-C16	1.512(8)	C35-C36	1.535(8)
C15-C19	1.522(8)	C35-H35	1.00
C15-H15	1.00	C36-C37	1.553(8)
C16-C17	1.532(8)	C36-H36	1.00
C16-H16	1.00	C37-C38	1.537(8)
C17-C18	1.541(8)	C37-H37	1.00
C17-H17	1.00	C38-H38A	0.99
C18-C19	1.524(8)	C38-H38B	0.99
C18-H18	1.00	C39-O5	1.431(6)
C19-H19A	0.99	C39-C40	1.519(7)
C19-H19B	0.99	C39-C51	1.530(7)
C20-O3	1.424(6)	C39-C49	1.607(7)
C20-C32	1.512(8)	C40-C41	1.369(8)
C20-C21	1.519(8)	C40-C50	1.409(8)

C41-C42	1.404(9)	C53-C54	1.505(8)
C41-H41	0.95	C53-C57	1.514(8)
C42-C43	1.381(9)	C53-H53	1.00
C42-H42	0.95	C54-C55	1.519(7)
C43-C44	1.419(8)	C54-H54	1.00
C43-H43	0.95	C55-C56	1.546(7)
C44-C50	1.400(8)	C55-H55	1.00
C44-C45	1.419(8)	C56-C57	1.524(8)
C45-C46	1.377(9)	C56-H56	1.00
C45-H45	0.95	C57-H57A	0.99
C46-C47	1.431(8)	C57-H57B	0.99
C46-H46	0.95	C58-Cl1#1	1.780(6)
C47-C48	1.355(8)	C58-Cl1	1.780(6)
C47-H47	0.95	C58-H58A	1.07(7)
C48-C50	1.417(8)	C59-Cl2	1.769(5)
C48-C49	1.518(7)	C59-Cl2#2	1.769(5)
C49-O6	1.422(6)	C59-H59A	1.10(7)
C49-C55	1.523(7)	O1-H1O	0.84
C51-C52	1.526(8)	O2-H2O	0.84
C51-C56	1.559(8)	O5-H5O	0.84
C51-H51	1.00	O6-H6O	0.84
C52-C53	1.521(8)	O3-H3O	0.84
C52-C54	1.535(8)	O4-H4O	0.84
C52-H52	1.00		

O1-C1-C2	112.2(4)	C8-C7-C6	120.0(5)
O1-C1-C13	110.3(4)	C8-C7-H7	120.0
C2-C1-C13	113.1(4)	C6-C7-H7	120.0
O1-C1-C11	113.8(4)	C7-C8-C9	122.3(6)
C2-C1-C11	104.3(4)	C7-C8-H8	118.8
C13-C1-C11	102.8(4)	C9-C8-H8	118.8
C3-C2-C12	119.9(5)	C10-C9-C8	118.8(6)
C3-C2-C1	131.1(5)	C10-C9-H9	120.6
C12-C2-C1	108.9(5)	C8-C9-H9	120.6
C2-C3-C4	117.6(6)	C9-C10-C12	118.6(5)
C2-C3-H3	121.2	C9-C10-C11	131.2(5)
C4-C3-H3	121.2	C12-C10-C11	110.0(5)
C5-C4-C3	122.7(6)	O2-C11-C10	111.5(4)
C5-C4-H4	118.7	O2-C11-C17	109.1(4)
C3-C4-H4	118.7	C10-C11-C17	114.9(4)
C4-C5-C6	120.1(5)	O2-C11-C1	114.9(4)
C4-C5-H5	119.9	C10-C11-C1	104.0(4)
C6-C5-H5	119.9	C17-C11-C1	102.2(4)
C12-C6-C7	115.7(6)	C6-C12-C10	124.5(5)
C12-C6-C5	116.7(5)	C6-C12-C2	122.9(5)
C7-C6-C5	127.5(5)	C10-C12-C2	112.6(5)

C1-C13-C14	111.1(4)	C32-C20-C30	102.6(4)
C1-C13-C18	103.9(4)	C21-C20-C30	103.7(4)
C14-C13-C18	97.1(4)	C22-C21-C31	119.7(5)
C1-C13-H13	114.4	C22-C21-C20	130.8(5)
C14-C13-H13	114.4	C31-C21-C20	109.4(5)
C18-C13-H13	114.4	C21-C22-C23	118.0(5)
C15-C14-C16	59.7(4)	C21-C22-H22	121.0
C15-C14-C13	108.0(4)	C23-C22-H22	121.0
C16-C14-C13	103.9(4)	C24-C23-C22	122.7(6)
C15-C14-H14	122.8	C24-C23-H23	118.7
C16-C14-H14	122.8	C22-C23-H23	118.7
C13-C14-H14	122.8	C23-C24-C25	120.4(5)
C14-C15-C16	60.7(4)	C23-C24-H24	119.8
C14-C15-C19	107.2(5)	C25-C24-H24	119.8
C16-C15-C19	107.2(5)	C24-C25-C31	116.0(5)
C14-C15-H15	122.0	C24-C25-C26	127.7(5)
C16-C15-H15	122.0	C31-C25-C26	116.3(5)
C19-C15-H15	122.0	C27-C26-C25	119.8(5)
C15-C16-C14	59.5(4)	C27-C26-H26	120.1
C15-C16-C17	108.1(5)	C25-C26-H26	120.1
C14-C16-C17	104.3(4)	C26-C27-C28	122.9(5)
C15-C16-H16	122.7	C26-C27-H27	118.6
C14-C16-H16	122.7	C28-C27-H27	118.6
C17-C16-H16	122.7	C29-C28-C27	118.2(5)
C16-C17-C11	109.8(4)	C29-C28-H28	120.9
C16-C17-C18	96.7(4)	C27-C28-H28	120.9
C11-C17-C18	104.2(4)	C28-C29-C31	119.2(5)
C16-C17-H17	114.8	C28-C29-C30	130.5(5)
C11-C17-H17	114.8	C31-C29-C30	110.3(5)
C18-C17-H17	114.8	O4-C30-C29	111.9(4)
C19-C18-C13	105.2(5)	O4-C30-C36	109.4(4)
C19-C18-C17	105.5(4)	C29-C30-C36	114.5(4)
C13-C18-C17	95.1(4)	O4-C30-C20	114.4(4)
C19-C18-H18	116.1	C29-C30-C20	103.6(4)
C13-C18-H18	116.1	C36-C30-C20	102.7(4)
C17-C18-H18	116.1	C29-C31-C21	113.0(5)
C15-C19-C18	96.7(4)	C29-C31-C25	123.6(5)
C15-C19-H19A	112.4	C21-C31-C25	123.3(5)
C18-C19-H19A	112.4	C20-C32-C33	110.3(4)
C15-C19-H19B	112.4	C20-C32-C37	104.2(4)
C18-C19-H19B	112.4	C33-C32-C37	97.6(4)
H19A-C19-H19B	110.0	C20-C32-H32	114.4
O3-C20-C32	110.4(4)	C33-C32-H32	114.4
O3-C20-C21	111.0(4)	C37-C32-H32	114.4
C32-C20-C21	114.4(4)	C34-C33-C35	60.3(4)
O3-C20-C30	114.4(4)	C34-C33-C32	107.7(5)

C35-C33-C32	103.8(5)	C43-C42-C41	122.4(6)
C34-C33-H33	122.8	C43-C42-H42	118.8
C35-C33-H33	122.8	C41-C42-H42	118.8
C32-C33-H33	122.8	C42-C43-C44	120.2(5)
C33-C34-C35	60.5(4)	C42-C43-H43	119.9
C33-C34-C38	107.7(5)	C44-C43-H43	119.9
C35-C34-C38	107.3(5)	C50-C44-C43	116.1(5)
C33-C34-H34	121.9	C50-C44-C45	116.4(5)
C35-C34-H34	121.9	C43-C44-C45	127.5(5)
C38-C34-H34	121.9	C46-C45-C44	120.3(5)
C34-C35-C33	59.2(4)	C46-C45-H45	119.8
C34-C35-C36	108.3(5)	C44-C45-H45	119.8
C33-C35-C36	105.2(5)	C45-C46-C47	121.8(5)
C34-C35-H35	122.4	C45-C46-H46	119.1
C33-C35-H35	122.4	C47-C46-H46	119.1
C36-C35-H35	122.4	C48-C47-C46	118.8(5)
C30-C36-C35	109.6(5)	C48-C47-H47	120.6
C30-C36-C37	102.8(4)	C46-C47-H47	120.6
C35-C36-C37	96.3(4)	C47-C48-C50	119.3(5)
C30-C36-H36	115.3	C47-C48-C49	131.9(5)
C35-C36-H36	115.3	C50-C48-C49	108.8(4)
C37-C36-H36	115.3	O6-C49-C48	112.2(4)
C32-C37-C38	104.4(5)	O6-C49-C55	110.2(4)
C32-C37-C36	95.6(4)	C48-C49-C55	113.7(4)
C38-C37-C36	105.0(4)	O6-C49-C39	113.4(4)
C32-C37-H37	116.4	C48-C49-C39	104.4(4)
C38-C37-H37	116.4	C55-C49-C39	102.5(4)
C36-C37-H37	116.4	C44-C50-C40	123.4(5)
C34-C38-C37	96.7(4)	C44-C50-C48	123.3(5)
C34-C38-H38A	112.4	C40-C50-C48	113.3(5)
C37-C38-H38A	112.4	C52-C51-C39	109.7(4)
C34-C38-H38B	112.4	C52-C51-C56	97.0(4)
C37-C38-H38B	112.4	C39-C51-C56	103.8(4)
H38A-C38-H38B	110.0	C52-C51-H51	114.8
O5-C39-C40	111.4(4)	C39-C51-H51	114.8
O5-C39-C51	109.2(4)	C56-C51-H51	114.8
C40-C39-C51	114.6(4)	C53-C52-C51	107.9(4)
O5-C39-C49	114.3(4)	C53-C52-C54	59.0(4)
C40-C39-C49	104.3(4)	C51-C52-C54	104.3(4)
C51-C39-C49	102.8(4)	C53-C52-H52	122.8
C41-C40-C50	119.3(5)	C51-C52-H52	122.8
C41-C40-C39	131.5(5)	C54-C52-H52	122.8
C50-C40-C39	109.1(4)	C54-C53-C57	107.8(5)
C40-C41-C42	118.6(6)	C54-C53-C52	61.0(4)
C40-C41-H41	120.7	C57-C53-C52	107.3(5)
C42-C41-H41	120.7	C54-C53-H53	121.8

C57-C53-H53	121.8	C51-C56-H56	116.6
C52-C53-H53	121.8	C53-C57-C56	97.1(4)
C53-C54-C55	107.9(5)	C53-C57-H57A	112.3
C53-C54-C52	60.0(4)	C56-C57-H57A	112.3
C55-C54-C52	103.9(4)	C53-C57-H57B	112.3
C53-C54-H54	122.8	C56-C57-H57B	112.3
C55-C54-H54	122.8	H57A-C57-H57B	109.9
C52-C54-H54	122.8	Cl1#1-C58-Cl1	109.7(5)
C54-C55-C49	111.0(4)	Cl1#1-C58-H58A	105(4)
C54-C55-C56	97.6(4)	Cl1-C58-H58A	113(4)
C49-C55-C56	104.2(4)	Cl2-C59-Cl2#2	110.7(5)
C54-C55-H55	114.2	Cl2-C59-H59A	104(4)
C49-C55-H55	114.2	Cl2#2-C59-H59A	105(4)
C56-C55-H55	114.2	C1-O1-H1O	109.5
C57-C56-C55	105.0(4)	C11-O2-H2O	109.5
C57-C56-C51	104.8(4)	C39-O5-H5O	109.5
C55-C56-C51	94.3(4)	C49-O6-H6O	109.5
C57-C56-H56	116.6	C20-O3-H3O	109.5
C55-C56-H56	116.6	C30-O4-H4O	109.5

Symmetry transformations used to generate equivalent atoms:
#1 x-y,-y,-z+4/3 #2 -x+2,-x+y+1,-z+5/3

Table 5.33. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5.4d.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	10(3)	14(3)	20(3)	1(2)	0(2)	5(2)
C2	14(3)	15(3)	19(3)	1(2)	2(2)	7(2)
C3	17(3)	20(3)	30(3)	0(3)	2(2)	7(2)
C4	20(3)	23(3)	37(4)	-10(3)	5(3)	9(3)
C5	21(3)	14(3)	43(4)	0(3)	4(3)	10(2)
C6	14(3)	17(3)	34(3)	4(2)	3(2)	9(2)
C7	20(3)	21(3)	49(4)	12(3)	8(3)	13(3)
C8	23(3)	30(3)	33(4)	12(3)	3(3)	16(3)
C9	16(3)	24(3)	28(3)	6(3)	-1(2)	8(3)
C10	6(2)	19(3)	29(3)	2(2)	1(2)	7(2)
C11	13(3)	15(3)	15(3)	-2(2)	2(2)	8(2)
C12	6(2)	15(3)	28(3)	2(2)	0(2)	4(2)
C13	15(3)	16(3)	20(3)	2(2)	3(2)	10(2)
C14	13(3)	14(3)	26(3)	2(2)	2(2)	7(2)
C15	15(3)	18(3)	35(4)	3(3)	5(3)	6(2)
C16	14(3)	16(3)	28(3)	-3(2)	-1(2)	6(2)
C17	11(3)	13(3)	25(3)	-3(2)	-3(2)	5(2)
C18	8(2)	15(3)	27(3)	-2(2)	-1(2)	6(2)
C19	14(3)	20(3)	22(3)	0(2)	-1(2)	6(2)
C20	19(3)	9(3)	20(3)	2(2)	1(2)	8(2)
C21	14(3)	15(3)	21(3)	3(2)	1(2)	9(2)
C22	25(3)	17(3)	18(3)	2(2)	0(2)	12(2)
C23	26(3)	19(3)	24(3)	4(2)	6(3)	11(3)
C24	17(3)	17(3)	34(3)	6(2)	6(3)	6(2)
C25	21(3)	13(3)	23(3)	-2(2)	0(2)	10(2)
C26	17(3)	13(3)	38(4)	-5(2)	-2(3)	8(2)
C27	21(3)	20(3)	25(3)	-8(2)	-9(2)	13(2)
C28	21(3)	20(3)	17(3)	-4(2)	0(2)	11(2)
C29	16(3)	14(3)	21(3)	1(2)	1(2)	9(2)
C30	14(3)	11(3)	20(3)	1(2)	3(2)	7(2)
C31	18(3)	17(3)	16(3)	-4(2)	-1(2)	13(2)
C32	16(3)	17(3)	21(3)	3(2)	-2(2)	7(2)
C33	15(3)	19(3)	27(3)	1(2)	-2(2)	9(2)
C34	14(3)	17(3)	40(4)	6(3)	4(3)	8(2)
C35	16(3)	15(3)	30(3)	5(2)	7(2)	5(2)
C36	15(3)	12(3)	25(3)	2(2)	4(2)	7(2)
C37	16(3)	15(3)	27(3)	6(2)	4(2)	8(2)
C38	22(3)	29(3)	41(4)	8(3)	7(3)	19(3)
C39	11(3)	11(3)	15(3)	2(2)	1(2)	2(2)
C40	13(3)	11(3)	14(3)	-1(2)	-2(2)	3(2)
C41	19(3)	13(3)	24(3)	-2(2)	-7(2)	3(2)

C42	25(3)	23(3)	26(3)	-2(3)	-10(3)	8(3)
C43	12(3)	16(3)	35(3)	-1(2)	-8(2)	4(2)
C44	12(3)	13(3)	30(3)	-1(2)	-2(2)	4(2)
C45	17(3)	18(3)	37(4)	-1(3)	6(3)	8(2)
C46	19(3)	22(3)	27(3)	3(2)	9(2)	9(2)
C47	20(3)	12(3)	23(3)	4(2)	3(2)	7(2)
C48	14(3)	10(3)	19(3)	2(2)	0(2)	4(2)
C49	10(3)	13(3)	14(3)	0(2)	-1(2)	3(2)
C50	12(3)	7(2)	23(3)	0(2)	-2(2)	-1(2)
C51	16(3)	11(3)	18(3)	-1(2)	0(2)	6(2)
C52	18(3)	17(3)	19(3)	0(2)	3(2)	8(2)
C53	24(3)	16(3)	25(3)	1(2)	-1(2)	13(2)
C54	14(3)	15(3)	25(3)	0(2)	2(2)	6(2)
C55	15(3)	16(3)	14(3)	-2(2)	-2(2)	8(2)
C56	15(3)	12(3)	24(3)	-2(2)	1(2)	5(2)
C57	22(3)	13(3)	24(3)	0(2)	1(2)	8(2)
C58	32(4)	48(6)	43(6)	0(5)	0(2)	24(3)
C59	51(6)	28(3)	30(5)	-2(2)	-3(4)	26(3)
Cl1	35(1)	33(1)	49(1)	-4(1)	-1(1)	13(1)
Cl2	34(1)	31(1)	37(1)	-1(1)	-6(1)	8(1)
O1	9(2)	22(2)	24(2)	3(2)	-1(2)	6(2)
O2	12(2)	23(2)	23(2)	-2(2)	2(2)	11(2)
O5	15(2)	10(2)	23(2)	7(2)	4(2)	2(2)
O6	14(2)	12(2)	23(2)	-2(2)	-5(2)	3(2)
O3	17(2)	15(2)	25(2)	-4(2)	-2(2)	8(2)
O4	22(2)	16(2)	23(2)	6(2)	2(2)	12(2)

Table 5.34. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5.4d**.

	x	y	z	U(eq)
H3	6589	2577	8273	28
H4	6636	4303	8271	33
H5	6637	5177	7769	31
H7	6584	5093	7087	34
H8	6493	4088	6603	33
H9	6362	2344	6640	28
H13	5192	324	8031	20
H14	5900	-1003	7823	21
H15	4022	-2390	7549	28
H16	5680	-1134	7160	24
H17	4847	119	6985	21
H18	4291	726	7528	20
H19A	3203	-1198	7778	24
H19B	3060	-1284	7366	24
H22	7738	-1383	8391	24
H23	6001	-3015	8464	28
H24	4942	-4036	8006	28
H26	4742	-4227	7326	27
H27	5518	-3439	6806	25
H28	7257	-1795	6765	22
H32	9881	-704	8044	22
H33	11112	1304	7801	24
H34	12342	765	7456	28
H35	10938	1143	7140	25
H36	9597	-959	6993	20
H37	9224	-2067	7550	23
H38A	11253	-1218	7712	34
H38B	11153	-1316	7299	34
H41	11831	3636	8263	25
H42	13444	3502	8238	32
H43	14197	3386	7723	27
H45	14035	3333	7044	29
H46	13007	3291	6575	27
H47	11329	3333	6638	22
H51	11019	5107	7975	18
H52	8905	4317	7855	22
H53	9241	5993	7482	25
H54	8648	4119	7191	22
H55	10605	4796	6930	18
H56	12054	5680	7402	21
H57A	11334	6916	7619	24

H57B	11181	6799	7207	24
H1O	7965	1960	7780	28
H2O	7790	1698	7114	28
H5O	9641	2192	7857	27
H6O	9404	1998	7223	27
H3O	8232	516	7868	29
H4O	7999	257	7151	29
H59A	10130(60)	-3610(60)	8083(18)	50(20)
H58A	1860(60)	0(60)	6892(17)	41(19)

Table 5.35. Torsion angles [°] for **5.4d**.

O1-C1-C2-C3	-56.0(8)	C1-C2-C12-C10	2.2(6)
C13-C1-C2-C3	69.5(7)	O1-C1-C13-C14	-53.1(6)
C11-C1-C2-C3	-179.6(5)	C2-C1-C13-C14	-179.6(4)
O1-C1-C2-C12	120.2(5)	C11-C1-C13-C14	68.5(5)
C13-C1-C2-C12	-114.2(5)	O1-C1-C13-C18	-156.5(4)
C11-C1-C2-C12	-3.3(6)	C2-C1-C13-C18	77.0(5)
C12-C2-C3-C4	1.0(8)	C11-C1-C13-C18	-34.8(5)
C1-C2-C3-C4	176.9(6)	C1-C13-C14-C15	-132.7(5)
C2-C3-C4-C5	-2.0(9)	C18-C13-C14-C15	-24.9(5)
C3-C4-C5-C6	1.6(9)	C1-C13-C14-C16	-70.5(5)
C4-C5-C6-C12	0.0(8)	C18-C13-C14-C16	37.4(5)
C4-C5-C6-C7	-177.2(6)	C13-C14-C15-C16	95.9(5)
C12-C6-C7-C8	0.7(8)	C16-C14-C15-C19	-100.5(5)
C5-C6-C7-C8	177.9(6)	C13-C14-C15-C19	-4.6(6)
C6-C7-C8-C9	0.0(9)	C19-C15-C16-C14	100.5(5)
C7-C8-C9-C10	0.3(9)	C14-C15-C16-C17	-96.3(5)
C8-C9-C10-C12	-1.3(8)	C19-C15-C16-C17	4.1(6)
C8-C9-C10-C11	-176.6(5)	C13-C14-C16-C15	-102.9(5)
C9-C10-C11-O2	49.2(8)	C15-C14-C16-C17	102.8(5)
C12-C10-C11-O2	-126.5(5)	C13-C14-C16-C17	-0.1(5)
C9-C10-C11-C17	-75.6(7)	C15-C16-C17-C11	132.9(5)
C12-C10-C11-C17	108.8(5)	C14-C16-C17-C11	70.7(5)
C9-C10-C11-C1	173.6(5)	C15-C16-C17-C18	25.1(5)
C12-C10-C11-C1	-2.1(5)	C14-C16-C17-C18	-37.1(5)
O1-C1-C11-O2	2.8(6)	O2-C11-C17-C16	51.5(6)
C2-C1-C11-O2	125.3(4)	C10-C11-C17-C16	177.4(5)
C13-C1-C11-O2	-116.4(5)	C1-C11-C17-C16	-70.6(5)
O1-C1-C11-C10	-119.3(5)	O2-C11-C17-C18	154.2(4)
C2-C1-C11-C10	3.2(5)	C10-C11-C17-C18	-79.9(5)
C13-C1-C11-C10	121.5(4)	C1-C11-C17-C18	32.1(5)
O1-C1-C11-C17	120.8(4)	C1-C13-C18-C19	161.0(4)
C2-C1-C11-C17	-116.6(4)	C14-C13-C18-C19	47.1(5)
C13-C1-C11-C17	1.6(5)	C1-C13-C18-C17	53.4(5)
C7-C6-C12-C10	-1.8(8)	C14-C13-C18-C17	-60.5(4)
C5-C6-C12-C10	-179.3(5)	C16-C17-C18-C19	-47.2(5)
C7-C6-C12-C2	176.5(5)	C11-C17-C18-C19	-159.6(4)
C5-C6-C12-C2	-1.1(8)	C16-C17-C18-C13	60.1(4)
C9-C10-C12-C6	2.1(8)	C11-C17-C18-C13	-52.3(5)
C11-C10-C12-C6	178.4(5)	C14-C15-C19-C18	32.2(5)
C9-C10-C12-C2	-176.3(5)	C16-C15-C19-C18	-31.7(5)
C11-C10-C12-C2	0.0(6)	C13-C18-C19-C15	-50.0(5)
C3-C2-C12-C6	0.5(8)	C17-C18-C19-C15	49.8(5)
C1-C2-C12-C6	-176.2(5)	O3-C20-C21-C22	-53.2(7)
C3-C2-C12-C10	179.0(5)	C32-C20-C21-C22	72.5(7)

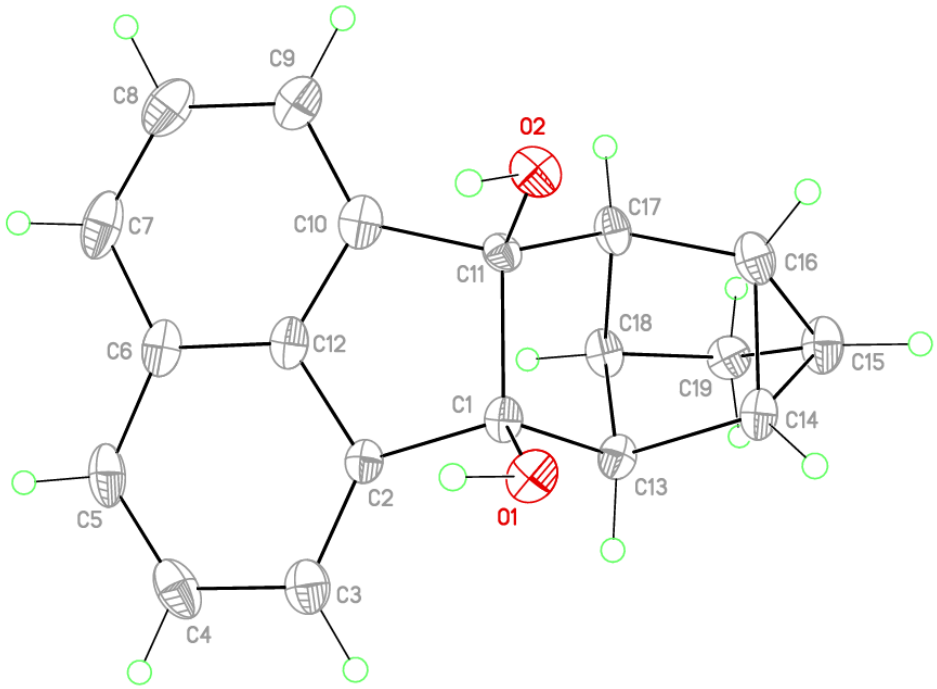
C30-C20-C21-C22	-176.6(5)	O3-C20-C32-C37	-156.0(4)
O3-C20-C21-C31	123.8(5)	C21-C20-C32-C37	78.0(5)
C32-C20-C21-C31	-110.5(5)	C30-C20-C32-C37	-33.6(5)
C30-C20-C21-C31	0.5(5)	C20-C32-C33-C34	-134.0(5)
C31-C21-C22-C23	0.8(8)	C37-C32-C33-C34	-25.7(6)
C20-C21-C22-C23	177.6(5)	C20-C32-C33-C35	-71.2(6)
C21-C22-C23-C24	-0.6(9)	C37-C32-C33-C35	37.1(5)
C22-C23-C24-C25	-0.1(9)	C32-C33-C34-C35	96.1(5)
C23-C24-C25-C31	0.7(8)	C35-C33-C34-C38	-100.3(5)
C23-C24-C25-C26	-177.6(6)	C32-C33-C34-C38	-4.2(6)
C24-C25-C26-C27	176.8(5)	C38-C34-C35-C33	100.9(5)
C31-C25-C26-C27	-1.5(8)	C33-C34-C35-C36	-97.2(5)
C25-C26-C27-C28	0.6(9)	C38-C34-C35-C36	3.7(6)
C26-C27-C28-C29	0.6(8)	C32-C33-C35-C34	-102.7(5)
C27-C28-C29-C31	-0.9(8)	C34-C33-C35-C36	102.6(5)
C27-C28-C29-C30	-177.8(5)	C32-C33-C35-C36	-0.1(6)
C28-C29-C30-O4	53.2(8)	O4-C30-C36-C35	53.7(6)
C31-C29-C30-O4	-123.9(5)	C29-C30-C36-C35	-179.8(5)
C28-C29-C30-C36	-72.0(7)	C20-C30-C36-C35	-68.3(5)
C31-C29-C30-C36	110.8(5)	O4-C30-C36-C37	155.2(4)
C28-C29-C30-C20	177.0(5)	C29-C30-C36-C37	-78.2(6)
C31-C29-C30-C20	-0.2(6)	C20-C30-C36-C37	33.3(5)
O3-C20-C30-O4	0.9(6)	C34-C35-C36-C30	131.8(5)
C32-C20-C30-O4	-118.7(5)	C33-C35-C36-C30	69.7(6)
C21-C20-C30-O4	121.9(5)	C34-C35-C36-C37	25.8(5)
O3-C20-C30-C29	-121.2(5)	C33-C35-C36-C37	-36.2(5)
C32-C20-C30-C29	119.2(4)	C20-C32-C37-C38	160.6(4)
C21-C20-C30-C29	-0.2(5)	C33-C32-C37-C38	47.3(5)
O3-C20-C30-C36	119.3(5)	C20-C32-C37-C36	53.5(5)
C32-C20-C30-C36	-0.2(5)	C33-C32-C37-C36	-59.8(5)
C21-C20-C30-C36	-119.6(4)	C30-C36-C37-C32	-52.8(5)
C28-C29-C31-C21	-177.1(5)	C35-C36-C37-C32	58.9(5)
C30-C29-C31-C21	0.5(6)	C30-C36-C37-C38	-159.4(5)
C28-C29-C31-C25	-0.1(8)	C35-C36-C37-C38	-47.6(5)
C30-C29-C31-C25	177.5(5)	C33-C34-C38-C37	31.9(6)
C22-C21-C31-C29	176.8(5)	C35-C34-C38-C37	-31.8(6)
C20-C21-C31-C29	-0.6(6)	C32-C37-C38-C34	-49.7(5)
C22-C21-C31-C25	-0.2(8)	C36-C37-C38-C34	50.2(6)
C20-C21-C31-C25	-177.6(5)	O5-C39-C40-C41	-52.5(7)
C24-C25-C31-C29	-177.2(5)	C51-C39-C40-C41	72.2(7)
C26-C25-C31-C29	1.3(8)	C49-C39-C40-C41	-176.2(5)
C24-C25-C31-C21	-0.6(8)	O5-C39-C40-C50	126.0(5)
C26-C25-C31-C21	177.9(5)	C51-C39-C40-C50	-109.3(5)
O3-C20-C32-C33	-52.2(6)	C49-C39-C40-C50	2.3(5)
C21-C20-C32-C33	-178.2(5)	C50-C40-C41-C42	-0.1(8)
C30-C20-C32-C33	70.2(5)	C39-C40-C41-C42	178.3(5)

C40-C41-C42-C43	0.3(9)	C49-C39-C51-C52	70.1(5)
C41-C42-C43-C44	-0.2(9)	O5-C39-C51-C56	-154.4(4)
C42-C43-C44-C50	0.0(8)	C40-C39-C51-C56	79.8(5)
C42-C43-C44-C45	-179.6(6)	C49-C39-C51-C56	-32.7(5)
C50-C44-C45-C46	-1.8(8)	C39-C51-C52-C53	-132.0(5)
C43-C44-C45-C46	177.8(5)	C56-C51-C52-C53	-24.6(5)
C44-C45-C46-C47	-0.3(9)	C39-C51-C52-C54	-70.4(5)
C45-C46-C47-C48	1.8(9)	C56-C51-C52-C54	37.0(5)
C46-C47-C48-C50	-1.0(8)	C51-C52-C53-C54	96.2(5)
C46-C47-C48-C49	-179.2(5)	C51-C52-C53-C57	-4.9(6)
C47-C48-C49-O6	56.6(7)	C54-C52-C53-C57	-101.1(5)
C50-C48-C49-O6	-121.7(5)	C57-C53-C54-C55	4.3(6)
C47-C48-C49-C55	-69.2(7)	C52-C53-C54-C55	-96.1(5)
C50-C48-C49-C55	112.4(5)	C57-C53-C54-C52	100.3(5)
C47-C48-C49-C39	179.9(5)	C51-C52-C54-C53	-102.6(5)
C50-C48-C49-C39	1.5(5)	C53-C52-C54-C55	102.8(5)
O5-C39-C49-O6	-1.7(6)	C51-C52-C54-C55	0.3(5)
C40-C39-C49-O6	120.2(5)	C53-C54-C55-C49	133.1(5)
C51-C39-C49-O6	-119.9(4)	C52-C54-C55-C49	70.5(5)
O5-C39-C49-C48	-124.2(5)	C53-C54-C55-C56	24.7(5)
C40-C39-C49-C48	-2.3(5)	C52-C54-C55-C56	-37.9(5)
C51-C39-C49-C48	117.6(4)	O6-C49-C55-C54	52.0(6)
O5-C39-C49-C55	117.1(5)	C48-C49-C55-C54	178.9(4)
C40-C39-C49-C55	-121.0(4)	C39-C49-C55-C54	-69.0(5)
C51-C39-C49-C55	-1.2(5)	O6-C49-C55-C56	156.0(4)
C43-C44-C50-C40	0.2(8)	C48-C49-C55-C56	-77.0(5)
C45-C44-C50-C40	179.8(5)	C39-C49-C55-C56	35.0(5)
C43-C44-C50-C48	-176.9(5)	C54-C55-C56-C57	-46.2(5)
C45-C44-C50-C48	2.7(8)	C49-C55-C56-C57	-160.2(4)
C41-C40-C50-C44	-0.2(8)	C54-C55-C56-C51	60.4(4)
C39-C40-C50-C44	-178.9(5)	C49-C55-C56-C51	-53.6(5)
C41-C40-C50-C48	177.3(5)	C52-C51-C56-C57	46.9(5)
C39-C40-C50-C48	-1.5(6)	C39-C51-C56-C57	159.2(4)
C47-C48-C50-C44	-1.3(8)	C52-C51-C56-C55	-59.8(4)
C49-C48-C50-C44	177.3(5)	C39-C51-C56-C55	52.5(5)
C47-C48-C50-C40	-178.7(5)	C54-C53-C57-C56	-31.6(6)
C49-C48-C50-C40	-0.1(6)	C52-C53-C57-C56	32.7(5)
O5-C39-C51-C52	-51.6(6)	C55-C56-C57-C53	48.7(5)
C40-C39-C51-C52	-177.4(4)	C51-C56-C57-C53	-50.0(5)

Table 5.36. Hydrogen bonds for **5.4d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1O...O5	0.84	2.04	2.744(5)	140.3
O2-H2O...O6	0.84	1.96	2.749(5)	156.6
O5-H5O...O3	0.84	1.99	2.752(5)	150.3
O6-H6O...O4	0.84	1.98	2.712(5)	145.5
O3-H3O...O1	0.84	1.98	2.729(5)	148.0
O4-H4O...O2	0.84	2.05	2.751(5)	140.2

Figure 5.6. View of **5.4d** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **5.4e**-CH_2Cl_2

X-ray Experimental for $C_{22}H_{23}NO_5$ - CH_2Cl_2: Crystals grew as clear, colorless prisms by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.33 x 0.24 x 0.24 mm. The data were collected at -173 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 700 low-temperature device. A total of 1401 frames of data were collected using λ-scans with a scan range of 0.8° and a counting time of 17 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.[42] The structure was solved by direct methods using SHELXT[30] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[31] Structure analysis was aided by use of the programs PLATON[32] and WinGX.[9] The hydrogen atoms bound to carbon atoms were calculated in idealized positions. The hydrogen atoms on the oxygen atoms O4 and O5 were observed in a ΔF map and refined with isotropic displacement parameters.

The function, $\Sigma w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sum(Fo))^2 + (0.0493*P)^2 + (0.372*P)]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. Rw(F2) refined to 0.0966, with R(F) equal to 0.0349 and a goodness of fit, S, = 1.05. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[34] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[35] All figures were generated using

SHELXTL/PC.[36] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 5.37. Crystal data and structure refinement for **5.4e**.

Empirical formula	C23 H25 Cl2 N O5	
Formula weight	466.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.321(2) Å	α= 88.415(6)°.
	b = 10.258(3) Å	β= 81.415(5)°.
	c = 12.729(3) Å	γ = 78.314(5)°.
Volume	1052.1(5) $Å^3$	
Z	2	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	0.346 mm^{-1}	
F(000)	488	
Crystal size	0.330 x 0.240 x 0.240 mm^3	
Theta range for data collection	1.618 to 28.269°.	
Index ranges	-11<=h<=11, -13<=k<=13, -16<=l<=16	
Reflections collected	17340	
Independent reflections	5155 [R(int) = 0.0387]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.861	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5155 / 0 / 289	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0927	
R indices (all data)	R1 = 0.0421, wR2 = 0.0966	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.471 and -0.296 $e.Å^{-3}$	

Table 5.38. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5.4e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	3612(2)	5209(1)	1405(1)	12(1)
C2	4192(2)	4152(1)	2187(1)	10(1)
C3	2925(2)	3258(1)	2496(1)	11(1)
C4	3364(2)	2384(1)	3442(1)	10(1)
C5	1922(2)	1727(1)	3929(1)	12(1)
C6	2501(2)	685(1)	4738(1)	13(1)
C7	1234(2)	893(1)	5734(1)	15(1)
C8	2774(2)	1486(1)	5662(1)	13(1)
C9	2326(2)	2933(1)	5314(1)	12(1)
C10	3632(2)	3232(1)	4408(1)	10(1)
C11	3363(2)	4721(1)	4155(1)	10(1)
C12	4507(2)	4930(1)	3132(1)	10(1)
C13	4225(2)	6372(1)	2785(1)	11(1)
C14	-176(2)	2004(1)	5516(1)	17(1)
C15	856(2)	2776(1)	4739(1)	13(1)
C16	3320(2)	7670(1)	1216(1)	13(1)
C17	4205(2)	7792(1)	226(1)	14(1)
C18	3789(2)	8926(1)	-378(1)	15(1)
C19	2497(2)	9939(1)	37(1)	18(1)
C20	1647(2)	9827(2)	1051(1)	32(1)
C21	2048(2)	8691(2)	1637(1)	28(1)
C22	2616(2)	11115(1)	-1591(1)	26(1)
C23	9172(2)	3685(2)	1135(1)	22(1)
N1	3716(1)	6452(1)	1794(1)	12(1)
O1	3120(1)	5051(1)	577(1)	17(1)
O2	1979(2)	11090(1)	-484(1)	27(1)
O3	4386(1)	7328(1)	3277(1)	15(1)
O4	4825(1)	1430(1)	3071(1)	13(1)
O5	5303(1)	2791(1)	4604(1)	12(1)
Cl1	8823(1)	5386(1)	1480(1)	34(1)
Cl2	8559(1)	2748(1)	2258(1)	23(1)

Table 5.39. Bond lengths [Å] and angles [°] for **5.4e**.

C1-O1	1.2120(16)	C12-C13	1.5142(16)
C1-N1	1.4029(17)	C12-H12	1.00
C1-C2	1.5071(16)	C13-O3	1.2175(16)
C2-C3	1.5345(17)	C13-N1	1.3852(16)
C2-C12	1.5455(17)	C14-C15	1.5232(17)
C2-H2	1.00	C14-H14A	0.99
C3-C4	1.5250(16)	C14-H14B	0.99
C3-H3A	0.99	C15-H15	1.00
C3-H3B	0.99	C16-C17	1.3776(17)
C4-O4	1.4251(15)	C16-C21	1.3850(19)
C4-C5	1.5361(17)	C16-N1	1.4370(15)
C4-C10	1.5923(17)	C17-C18	1.3889(17)
C5-C6	1.5211(17)	C17-H17	0.95
C5-C15	1.5526(17)	C18-C19	1.3869(19)
C5-H5	1.00	C18-H18	0.95
C6-C7	1.5136(17)	C19-O2	1.3619(15)
C6-C8	1.5231(18)	C19-C20	1.390(2)
C6-H6	1.00	C20-C21	1.3771(19)
C7-C14	1.5132(18)	C20-H20	0.95
C7-C8	1.5161(18)	C21-H21	0.95
C7-H7	1.00	C22-O2	1.4307(17)
C8-C9	1.5260(17)	C22-H22A	0.98
C8-H8	1.00	C22-H22B	0.98
C9-C10	1.5310(16)	C22-H22C	0.98
C9-C15	1.5521(18)	C23-Cl1	1.7670(16)
C9-H9	1.00	C23-Cl2	1.7704(15)
C10-O5	1.4290(15)	C23-H23A	0.99
C10-C11	1.5316(16)	C23-H23B	0.99
C11-C12	1.5309(16)	O4-H4O	0.84(2)
C11-H11A	0.99	O5-H5O	0.83(2)
C11-H11B	0.99		

O1-C1-N1	124.16(11)	C4-C3-H3B	109.5
O1-C1-C2	127.21(11)	C2-C3-H3B	109.5
N1-C1-C2	108.62(10)	H3A-C3-H3B	108.1
C1-C2-C3	111.71(10)	O4-C4-C3	106.85(10)
C1-C2-C12	104.65(10)	O4-C4-C5	112.30(10)
C3-C2-C12	113.61(10)	C3-C4-C5	111.52(10)
C1-C2-H2	108.9	O4-C4-C10	111.43(10)
C3-C2-H2	108.9	C3-C4-C10	112.06(10)
C12-C2-H2	108.9	C5-C4-C10	102.80(9)
C4-C3-C2	110.69(10)	C6-C5-C4	109.93(10)
C4-C3-H3A	109.5	C6-C5-C15	96.80(10)
C2-C3-H3A	109.5	C4-C5-C15	103.82(10)

C6-C5-H5	114.8	O3-C13-C12	127.33(11)
C4-C5-H5	114.8	N1-C13-C12	108.54(10)
C15-C5-H5	114.8	C7-C14-C15	96.97(10)
C7-C6-C5	108.15(10)	C7-C14-H14A	112.4
C7-C6-C8	59.90(8)	C15-C14-H14A	112.4
C5-C6-C8	104.55(10)	C7-C14-H14B	112.4
C7-C6-H6	122.6	C15-C14-H14B	112.4
C5-C6-H6	122.6	H14A-C14-H14B	109.9
C8-C6-H6	122.6	C14-C15-C9	104.80(10)
C14-C7-C6	107.64(10)	C14-C15-C5	105.44(10)
C14-C7-C8	107.20(10)	C9-C15-C5	94.73(9)
C6-C7-C8	60.36(8)	C14-C15-H15	116.4
C14-C7-H7	122.0	C9-C15-H15	116.4
C6-C7-H7	122.0	C5-C15-H15	116.4
C8-C7-H7	122.0	C17-C16-C21	120.61(12)
C7-C8-C6	59.74(8)	C17-C16-N1	118.83(11)
C7-C8-C9	107.96(10)	C21-C16-N1	120.55(11)
C6-C8-C9	104.37(10)	C16-C17-C18	120.17(12)
C7-C8-H8	122.7	C16-C17-H17	119.9
C6-C8-H8	122.7	C18-C17-H17	119.9
C9-C8-H8	122.7	C19-C18-C17	119.21(12)
C8-C9-C10	110.15(10)	C19-C18-H18	120.4
C8-C9-C15	96.77(10)	C17-C18-H18	120.4
C10-C9-C15	103.55(9)	O2-C19-C18	124.25(12)
C8-C9-H9	114.8	O2-C19-C20	115.49(12)
C10-C9-H9	114.8	C18-C19-C20	120.26(12)
C15-C9-H9	114.8	C21-C20-C19	120.17(13)
O5-C10-C9	114.01(9)	C21-C20-H20	119.9
O5-C10-C11	108.40(9)	C19-C20-H20	119.9
C9-C10-C11	111.35(10)	C20-C21-C16	119.52(13)
O5-C10-C4	107.98(9)	C20-C21-H21	120.2
C9-C10-C4	103.27(9)	C16-C21-H21	120.2
C11-C10-C4	111.77(9)	O2-C22-H22A	109.5
C12-C11-C10	108.92(10)	O2-C22-H22B	109.5
C12-C11-H11A	109.9	H22A-C22-H22B	109.5
C10-C11-H11A	109.9	O2-C22-H22C	109.5
C12-C11-H11B	109.9	H22A-C22-H22C	109.5
C10-C11-H11B	109.9	H22B-C22-H22C	109.5
H11A-C11-H11B	108.3	Cl1-C23-Cl2	109.87(8)
C13-C12-C11	112.07(10)	Cl1-C23-H23A	109.7
C13-C12-C2	105.07(9)	Cl2-C23-H23A	109.7
C11-C12-C2	111.87(10)	Cl1-C23-H23B	109.7
C13-C12-H12	109.2	Cl2-C23-H23B	109.7
C11-C12-H12	109.2	H23A-C23-H23B	108.2
C2-C12-H12	109.2	C13-N1-C1	112.88(10)
O3-C13-N1	124.12(11)	C13-N1-C16	124.24(11)

C1-N1-C16	122.88(10)	C4-O4-H4O	104.1(14)
C19-O2-C22	115.98(11)	C10-O5-H5O	107.5(13)

Table 5.40. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5.4e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	12(1)	11(1)	11(1)	2(1)	-1(1)	-1(1)
C2	11(1)	10(1)	9(1)	2(1)	-2(1)	-2(1)
C3	13(1)	12(1)	10(1)	2(1)	-3(1)	-4(1)
C4	12(1)	9(1)	9(1)	1(1)	-1(1)	-2(1)
C5	12(1)	11(1)	12(1)	1(1)	-2(1)	-4(1)
C6	15(1)	10(1)	14(1)	2(1)	0(1)	-4(1)
C7	17(1)	13(1)	15(1)	4(1)	2(1)	-6(1)
C8	16(1)	11(1)	11(1)	4(1)	-2(1)	-4(1)
C9	15(1)	10(1)	9(1)	1(1)	0(1)	-3(1)
C10	10(1)	10(1)	9(1)	2(1)	-2(1)	-2(1)
C11	13(1)	9(1)	9(1)	1(1)	-1(1)	-3(1)
C12	11(1)	9(1)	10(1)	2(1)	-2(1)	-2(1)
C13	10(1)	13(1)	9(1)	3(1)	0(1)	-3(1)
C14	14(1)	16(1)	20(1)	3(1)	3(1)	-5(1)
C15	11(1)	12(1)	15(1)	2(1)	1(1)	-2(1)
C16	18(1)	10(1)	10(1)	4(1)	-3(1)	-2(1)
C17	18(1)	12(1)	12(1)	0(1)	0(1)	0(1)
C18	20(1)	14(1)	10(1)	2(1)	0(1)	-3(1)
C19	30(1)	11(1)	13(1)	4(1)	-2(1)	0(1)
C20	43(1)	21(1)	19(1)	6(1)	11(1)	17(1)
C21	36(1)	22(1)	15(1)	9(1)	11(1)	10(1)
C22	44(1)	16(1)	13(1)	7(1)	-1(1)	0(1)
C23	24(1)	22(1)	18(1)	0(1)	-6(1)	2(1)
N1	16(1)	10(1)	9(1)	3(1)	-2(1)	-1(1)
O1	24(1)	15(1)	12(1)	2(1)	-7(1)	-2(1)
O2	45(1)	13(1)	14(1)	6(1)	2(1)	7(1)
O3	21(1)	13(1)	12(1)	2(1)	-4(1)	-7(1)
O4	14(1)	11(1)	12(1)	0(1)	0(1)	1(1)
O5	12(1)	15(1)	11(1)	3(1)	-4(1)	-2(1)
Cl1	45(1)	22(1)	34(1)	-1(1)	-6(1)	-6(1)
Cl2	17(1)	24(1)	26(1)	4(1)	-3(1)	2(1)

Table 5.41. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5.4e**.

	x	y	z	U(eq)
H2	5266	3589	1858	12
H3A	1804	3818	2680	14
H3B	2908	2687	1885	14
H5	1301	1418	3401	14
H6	3206	-205	4526	16
H7	1050	146	6229	18
H8	3672	1163	6104	15
H9	2032	3598	5906	14
H11A	2192	5063	4063	12
H11B	3614	5214	4748	12
H12	5688	4633	3248	12
H14A	-710	2527	6162	21
H14B	-1022	1677	5184	21
H15	241	3605	4435	16
H17	5102	7100	-45	17
H18	4382	9006	-1067	18
H20	787	10537	1340	39
H21	1456	8608	2326	34
H22A	3799	11141	-1677	39
H22B	2017	11908	-1917	39
H22C	2467	10315	-1937	39
H23A	10364	3360	871	27
H23B	8531	3573	560	27
H5O	5290(20)	2775(19)	5259(16)	29(5)
H4O	5450(30)	1450(20)	3527(17)	37(6)

Table 5.42. Torsion angles [°] for **5.4e**.

O1-C1-C2-C3	-51.43(17)	O4-C4-C10-C11	120.32(10)
N1-C1-C2-C3	128.11(11)	C3-C4-C10-C11	0.65(13)
O1-C1-C2-C12	-174.77(12)	C5-C4-C10-C11	-119.21(10)
N1-C1-C2-C12	4.77(13)	O5-C10-C11-C12	63.27(12)
C1-C2-C3-C4	-168.65(10)	C9-C10-C11-C12	-170.53(10)
C12-C2-C3-C4	-50.54(13)	C4-C10-C11-C12	-55.61(13)
C2-C3-C4-O4	-70.18(12)	C10-C11-C12-C13	175.87(9)
C2-C3-C4-C5	166.76(10)	C10-C11-C12-C2	58.17(12)
C2-C3-C4-C10	52.13(13)	C1-C2-C12-C13	-4.65(12)
O4-C4-C5-C6	50.28(13)	C3-C2-C12-C13	-126.75(10)
C3-C4-C5-C6	170.18(10)	C1-C2-C12-C11	117.18(10)
C10-C4-C5-C6	-69.58(11)	C3-C2-C12-C11	-4.93(14)
O4-C4-C5-C15	152.93(10)	C11-C12-C13-O3	60.55(16)
C3-C4-C5-C15	-87.18(11)	C2-C12-C13-O3	-177.76(12)
C10-C4-C5-C15	33.06(11)	C11-C12-C13-N1	-118.63(11)
C4-C5-C6-C7	132.63(11)	C2-C12-C13-N1	3.06(13)
C15-C5-C6-C7	25.22(12)	C6-C7-C14-C15	-31.12(13)
C4-C5-C6-C8	70.02(12)	C8-C7-C14-C15	32.47(13)
C15-C5-C6-C8	-37.38(11)	C7-C14-C15-C9	-50.32(12)
C5-C6-C7-C14	3.51(14)	C7-C14-C15-C5	48.96(12)
C8-C6-C7-C14	100.15(11)	C8-C9-C15-C14	47.44(11)
C5-C6-C7-C8	-96.64(11)	C10-C9-C15-C14	160.11(10)
C14-C7-C8-C6	-100.88(11)	C8-C9-C15-C5	-59.90(10)
C14-C7-C8-C9	-4.39(14)	C10-C9-C15-C5	52.77(10)
C6-C7-C8-C9	96.48(11)	C6-C5-C15-C14	-46.74(12)
C5-C6-C8-C7	102.79(11)	C4-C5-C15-C14	-159.25(10)
C7-C6-C8-C9	-102.65(11)	C6-C5-C15-C9	60.04(10)
C5-C6-C8-C9	0.14(12)	C4-C5-C15-C9	-52.47(10)
C7-C8-C9-C10	-132.35(11)	C21-C16-C17-C18	-2.4(2)
C6-C8-C9-C10	-69.98(12)	N1-C16-C17-C18	176.27(12)
C7-C8-C9-C15	-25.20(12)	C16-C17-C18-C19	1.3(2)
C6-C8-C9-C15	37.16(11)	C17-C18-C19-O2	-179.75(13)
C8-C9-C10-O5	-48.33(13)	C17-C18-C19-C20	0.9(2)
C15-C9-C10-O5	-150.90(10)	O2-C19-C20-C21	178.57(16)
C8-C9-C10-C11	-171.37(10)	C18-C19-C20-C21	-2.0(3)
C15-C9-C10-C11	86.07(11)	C19-C20-C21-C16	1.0(3)
C8-C9-C10-C4	68.55(12)	C17-C16-C21-C20	1.2(2)
C15-C9-C10-C4	-34.02(11)	N1-C16-C21-C20	-177.37(15)
O4-C4-C10-O5	1.18(12)	O3-C13-N1-C1	-179.28(12)
C3-C4-C10-O5	-118.48(10)	C12-C13-N1-C1	-0.07(14)
C5-C4-C10-O5	121.65(10)	O3-C13-N1-C16	0.34(19)
O4-C4-C10-C9	-119.89(10)	C12-C13-N1-C16	179.56(11)
C3-C4-C10-C9	120.45(10)	O1-C1-N1-C13	176.47(12)
C5-C4-C10-C9	0.58(11)	C2-C1-N1-C13	-3.09(14)

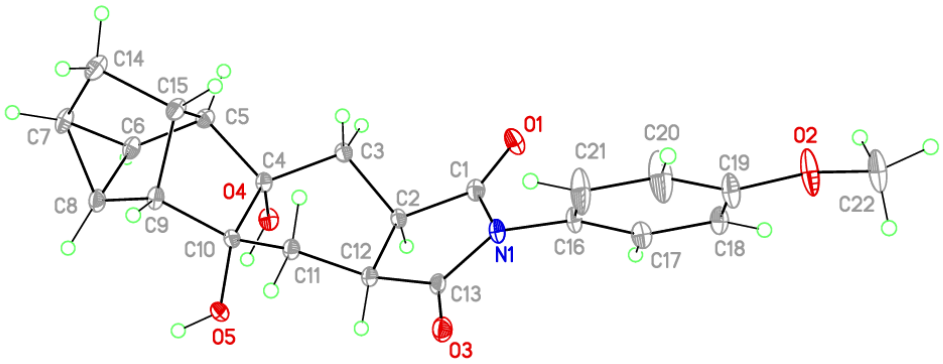
O1-C1-N1-C16	-3.16(19)	C17-C16-N1-C1	-59.69(17)
C2-C1-N1-C16	177.28(11)	C21-C16-N1-C1	118.93(16)
C17-C16-N1-C13	120.71(14)	C18-C19-O2-C22	12.1(2)
C21-C16-N1-C13	-60.66(19)	C20-C19-O2-C22	-168.50(1

Table 5.43. Hydrogen bonds for **5.4e** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C2-H2...Cl2	1.00	2.82	3.6418(15)	139.9
C5-H5...Cl2#1	1.00	2.97	3.7300(14)	133.9
C11-H11B...O5#2	0.99	2.60	3.4833(16)	149.1
C12-H12...Cl2	1.00	2.90	3.6852(14)	136.2
C17-H17...O1#3	0.95	2.44	3.3705(17)	164.8
C18-H18...O4#3	0.95	2.57	3.4541(17)	155.8
C20-H20...Cl2#4	0.95	2.78	3.7275(17)	173.3
C22-H22B...Cl1#5	0.98	2.77	3.5449(18)	136.2
C23-H23B...O1#3	0.99	2.38	3.1865(18)	138.0
O5-H5O...O3#2	0.83(2)	1.92(2)	2.7458(14)	171.4(19)
O4-H4O...O5	0.84(2)	1.94(2)	2.5543(14)	129.1(19)

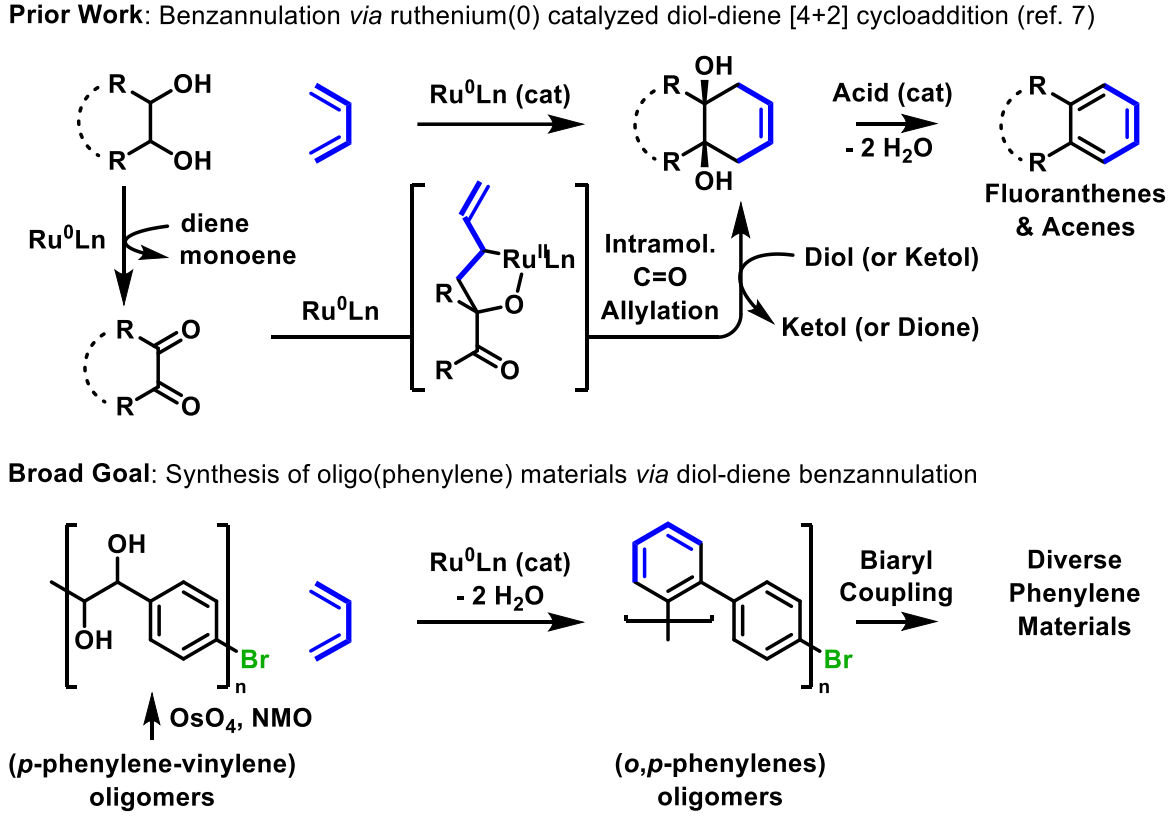
Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 -x+1,-y+1,-z+1 #3 -x+1,-y+1,-z
#4 x-1,y+1,z #5 -x+1,-y+2,-z

Figure 5.7. View of **5.4e** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Chapter 6. Helical Rod-Like Phenylene Cages *via* Ruthenium Catalyzed Diol-Diene Benzannulation: A Cord of Three Strands*

6.1 Introduction

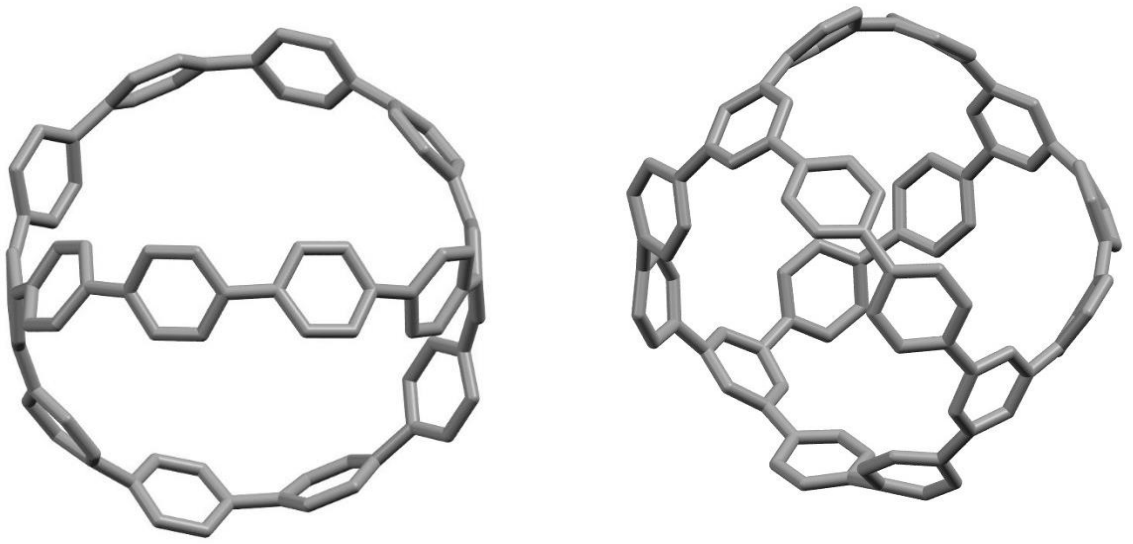


Scheme 6.1. Preparation of PAH materials via ruthenium catalyzed diol-diene benzannulation**.**

Oligophenylenes, which are comprised of conjugated phenylenes, are one of the important families in polycyclic aromatic hydrocarbons (PAHs).[1] Beyond their sheer aesthetic appeal[2] oligophenylenes have taken much attention because of their modular physical properties induced

* This chapter is based on the published work:
Sato, H.; Bender, J. A.; Roberts, S. T.; Krische, M. J. *J. Am. Chem. Soc.* **2018**, *140*, 2455.

Prior Work: Phenylene cages of spherical topology (ref. 9)



Itami, Segawa & Kamada (2013) Yamago (2013)

This Work: Phenylene cages of helical rod-like topology

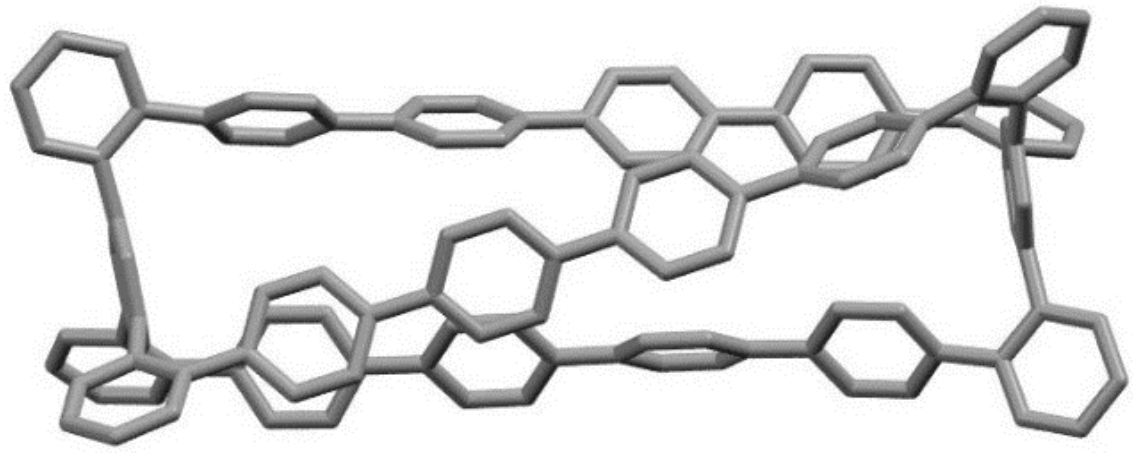


Figure 6.1.Phenylene cages of spherical and helical rod-like topology. Depicted structures are fully optimized by DFT calculations at the B3LYP/6-31G* level of theory.

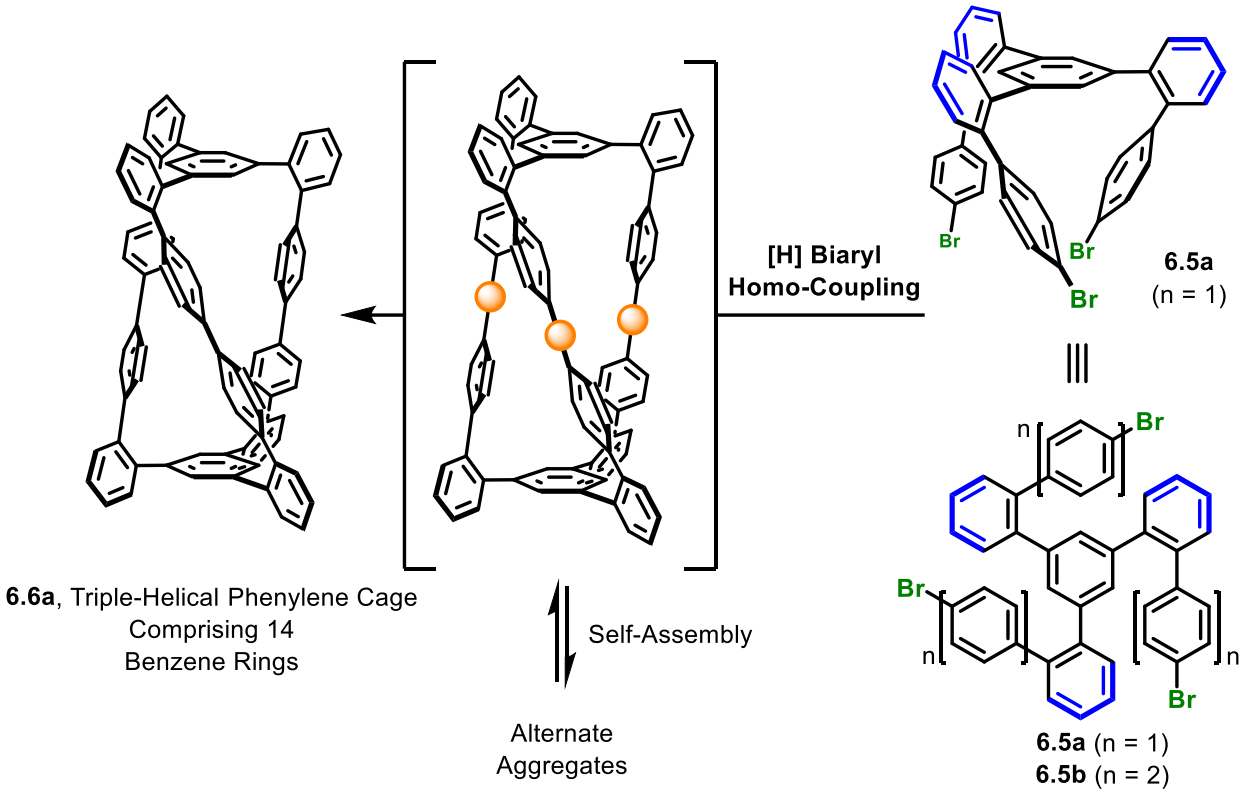
by their highly conjugated π-systems, which are applied to organic photovoltaic materials and semiconducters.[1] Moreover, their optical properties in aggregates and solid films provide interesting tests for electronic structure methods and molecular exciton theory.[3,4] Despite the growing interest of oligophenylenes to the field, there are relatively few catalytic synthetic methods for their preparation beyond classical biaryl crosscoupling.[1,5] Therefore, the development

of new protocols for oligophenylene construction is able to dramatically expand the PAH chemical space and have a broad impact on organomaterials chemistry.[6]

In connection with studies of alcohol-mediated C−C bond formation,[7] a ruthenium(0) catalyzed diene-diol [4+2] cycloaddition was developed in our laboratory.[8,9] The hexene diol cycloadducts from abundant diol starting materials are readily aromatized upon dehydration with a catalytic amount of acid to give acenes derivatives (Scheme 6.1).[8c] This process tolerates aryl halide functional groups, which can be further functionalized by conventional biaryl coupling reactions to provide highly conjugated π-systems. Herein, we demonstrate the synthesis of aryl halide through the benzannulation strategy and successive biaryl coupling with copper or nickel furnished modular syntheses of novel triple-helical phenylene cages of rod-like topology (Figure 1).[10,11]

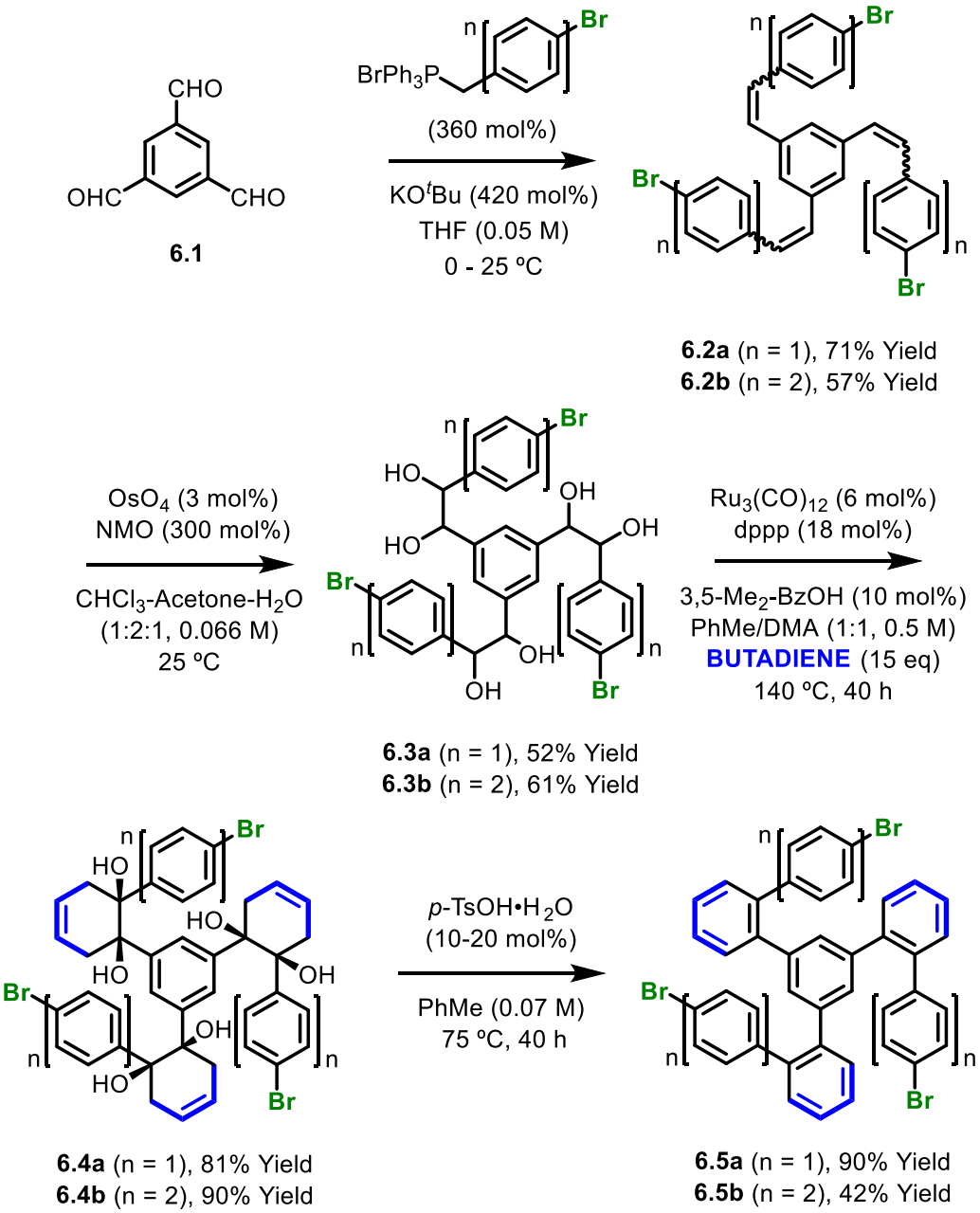
6.2 Results and Discussion

Retrosynthetically, we envisioned **6.6a** is partitioned into two symmetrical components, which are coupled by reductive biaryl homocoupling of a tris-bromide such as **6.5a** (Scheme 6.2). Ideally, self-assembly to form a discrete trimetallic coordination complex would enhance efficiency by suppressing the undesired productions of oligomeric products.[12] As demonstrated by Iyoda,[5c,13] Lipshutz cuprates [$Ar_2Cu(CN)Li_2$],[14] which incorporate a linear organocuprate Ar−Cu−Ar linkage generated from *t*-BuLi, CuCN and aryl bromide,[12,15] self-assembles in situ[16] to form the thermodynamically most stable intermediate. Successive reductive elimination induced by oxidant produce the macrocycle whose structure is expected from the intermediate. We envisioned that exploiting the linear organocuprate geometry and the ability of organocopper complexes to engage in self-assembly, rod-like phenylene cages might be achieved via 3-fold



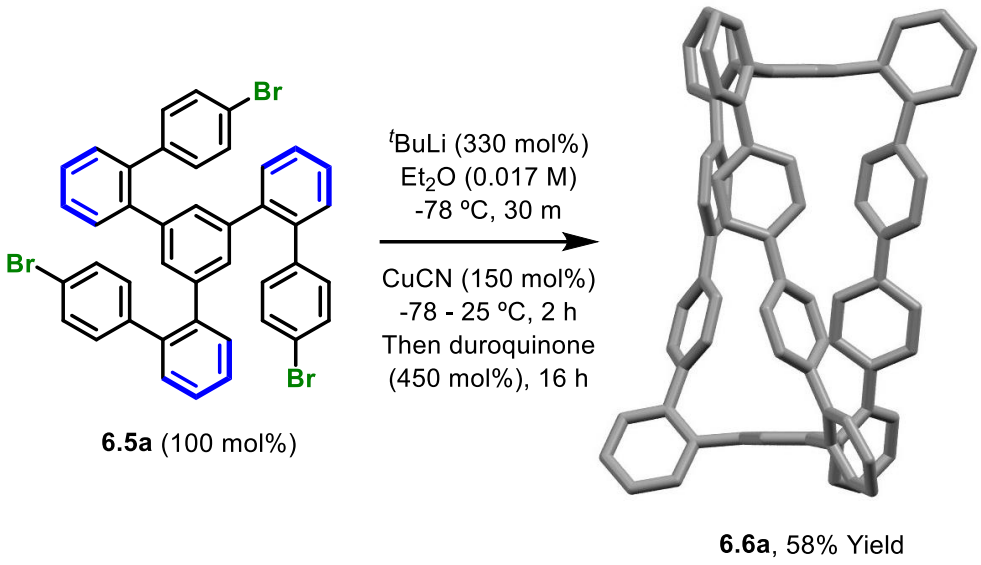
Scheme 6.2. Retrosynthetic analysis of rod-like phenylene cages via ruthenium(0) catalyzed diol-diene benzannulation and subsequent threefold reductive biaryl homocoupling.

copper-mediated homocoupling of a tris-bromide precursor such as **6.5a** and **6.5c**. The synthesis of tris-bromides **6.5a** and **6.5b** were achieved as follows using ruthenium catalyzed benzannulation reaction (Scheme 6.3).[17] 3-Fold Wittig olefination of benzene-1,3,5-tricarbaldehyde **6.1** gives trienes **6.2a** and **6.2b** in good yields as mixtures of stereoisomers with major (*Z*,*Z*,*Z*)-stereoisomer.[18] OsO_4 catalyzed dihydroxylation reaction with N-methylmorpholine N-Oxide (NMO)[19] converted trienes into the corresponding tris-diols **6.2a** and **6.2b**. Benzannulation of tris-diols **6.3a** and **6.3b** begins with the ruthenium(0) catalyzed cycloaddition with 1,3-butadiene.[8] 3-Fold cycloaddition occurred efficiently in the presence of a carboxylic acid cocatalyst to furnish the tris-cycloadducts **6.4a** and **6.4b** in 81% and 90% yields, respectively. Exposure of tris-cycloadducts **6.4a** and **6.4b** to substoichiometric quantities of *p*-toluenesulfonic acid (*p*-TsOH)



Scheme 6.3. Synthesis of tris-bromides **6.5a** and **6.5b** via ruthe-nium(0) catalyzed diol-diene benzannulation.[a] [a]Yields of material isolated by silica gel chromatography. See Supporting Information for further experimental details.

resulted in the tris-bromides **6.5a** and **6.5b** with aryl bromide tolerated. Then, tris-bromides **6.5a** and **6.5b** were subjected to 3-fold reductive biaryl homocoupling (Scheme 6.4). Tris-bromide **6.5a** was exposed to *t*-BuLi, followed by CuCN addition at -78 ˚C. Then, the reaction mixture was



Scheme 6.4. Copper-mediated reductive homo-coupling of tris-bromide **6.5a** to form rod-like phenylene cage **6.6a**.[a]

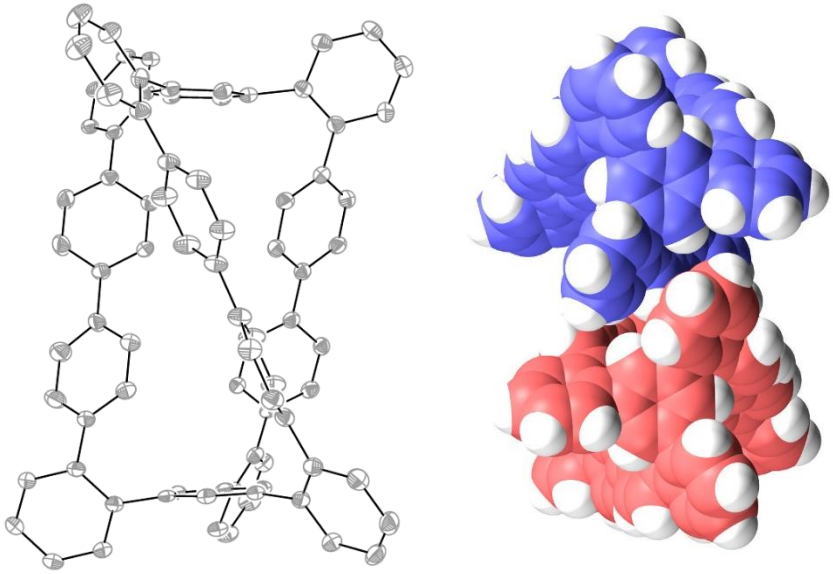
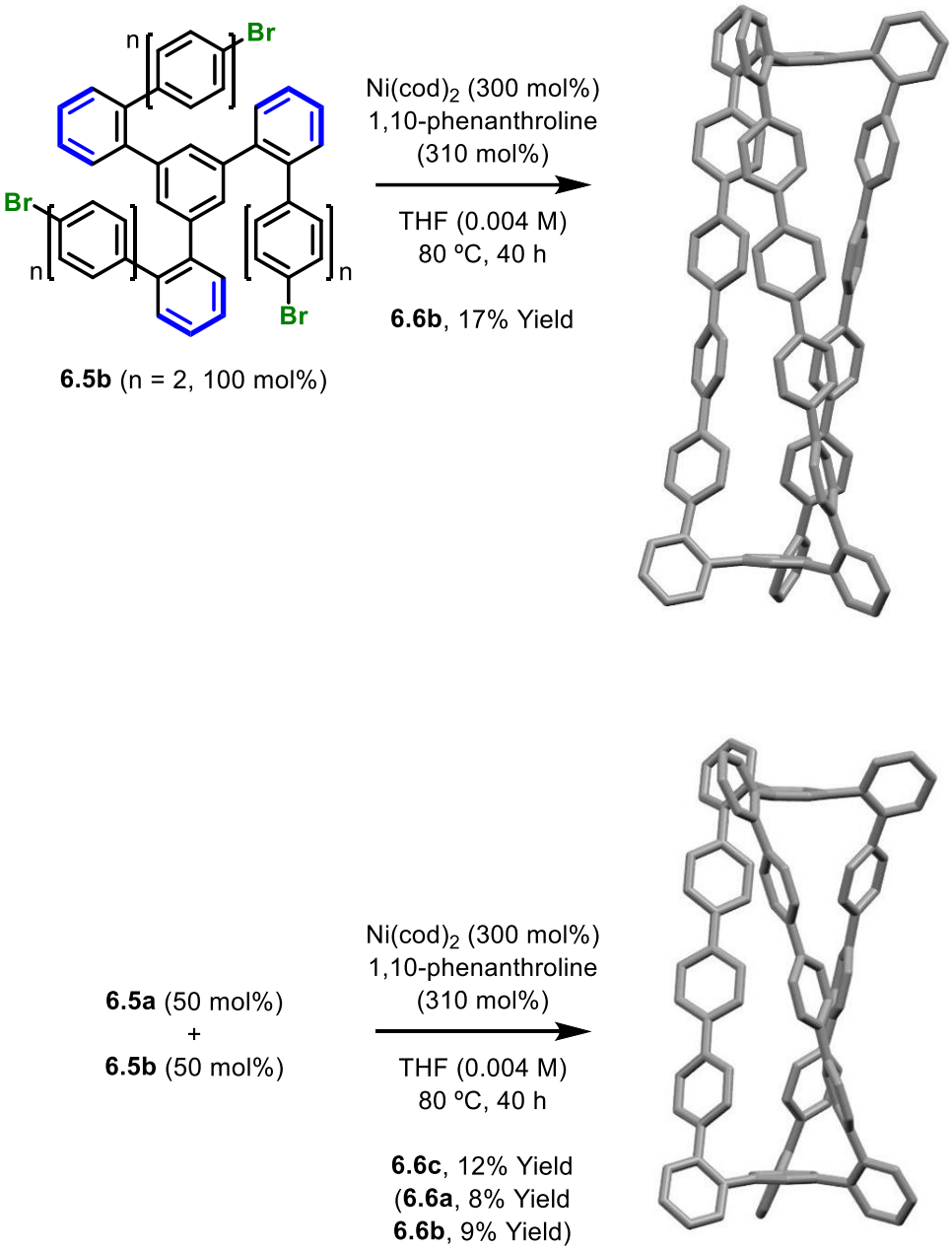


Figure 6.2. Left: Single-crystal X-ray diffraction data of triple helical phenylene cage **6.6a**. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms and solvent have been omitted for clarity. Right: Side-by-side packing of (P)- and (*M*)- helices as viewed down helical axis.

warmed up to ambient temperature and stirred for 2 hours for self-assembly process completion. To our delight, the desired triple helical phenylene cage **6.6a** was obtained in a remarkable 58% yield after purification by conventional silica column chromatography. Phenylene cage **6.6a** is

highly soluble in chlorinated solvents and could be characterized by 1H NMR, 13C NMR, high resolution MALDI-TOF mass spectrometry, as well as single crystal X-ray diffraction, which revealed a side-by-side packing of enantiomeric (*P*)- and (*M*)-helices in the solid state (Figure 6.2). The calculated and observed structures of **6.6a** were in a good accordance (Scheme 6.5 vs Figure 6.4).

Unfortunately, application of copper-mediated biaryl homocoupling conditions to **6.5b** was less efficient (9% yield) presumably due to its poor solubility in ethereal solvent under cryogenic conditions and perhaps a lower thermodynamic stability of the transient trimetallic organocuprate complex. Therefore, inspired by the work of Itami,[11e,f] nickel mediated 3-fold biaryl homocoupling of **6.5b** was attempted.[20] The reaction of **6.5b** with stoichiometric $Ni(cod)_2$ in the presence of 1,10-phenanthroline in highly diluted THF solvent condition to suppress polymerization at 80 °C led to the formation of the large phenylene cage **6.6b** in 17% yield after purification by GPC (Scheme 4). Phenylene cage **6.6b** was barely soluble in $CHCl_3$ and could be characterized by 1H NMR, 13C NMR and high resolution MALDI-TOF mass spectrometry. Finally, cross reductive coupling reaction between tris-bromides **6.5a** and **6.5b** was exposed to $Ni(cod)_2$ to obtain middle cage. The resulting mixture provided all sizes of the cages, which are separated by GPC separation method (For more information, see the experimental detail). Notably, attempted Suzuki cross-coupling of **6.5a** or **6.5b** with their corresponding tris-pinacol boronate esters (not shown) did not deliver **6.6a** or **6.6b** presumably because polymerization is favored to dimerization because of the large ring strains in palladium catalyzed cross coupling conditions.



Scheme 6.5. Nickel-mediated reductive homo-coupling of tris-bromide **6.5b** to form phenylene cage **6.6b** and cross-coupling of tris-bromides **6.5a** with **6.5b** to form phenylene cage **6.6c**,**6.6a.**

[a]Yield of material isolated by silica gel chromatography. Depicted structures of phenylene cages 6.6b and 6.6c are fully optimized by DFT calculations at the B3LYP/6-31G* level of theory.

6.3 Physical Measurements and Calculations

As a preliminary investigation of the potential utility of cages **6.6a**, **6.6c**, and **6.6b** for electronics applications, their steady-state absorption and emission properties were examined (Figure 6.3). The absorption spectra of these compounds are largely feature-less, displaying a prominent peak near ~300 nm and a second transition whose center falls <250 nm. These two transitions are reminiscent of absorption spectra of oligophenylenes and 1,3,5-triphenylbenzene, which display broad, featureless absorption bands peaked near ~295 and 250 nm, respectively.[21] This suggests the lowest energy transition is associated with absorption along the oligophenylenes walls of each cage while the higher energy transition arises from 1,3,5-triphenylbenzene moiety at their top and bottom. TDDFT calculations of the valence states of each molecule support this

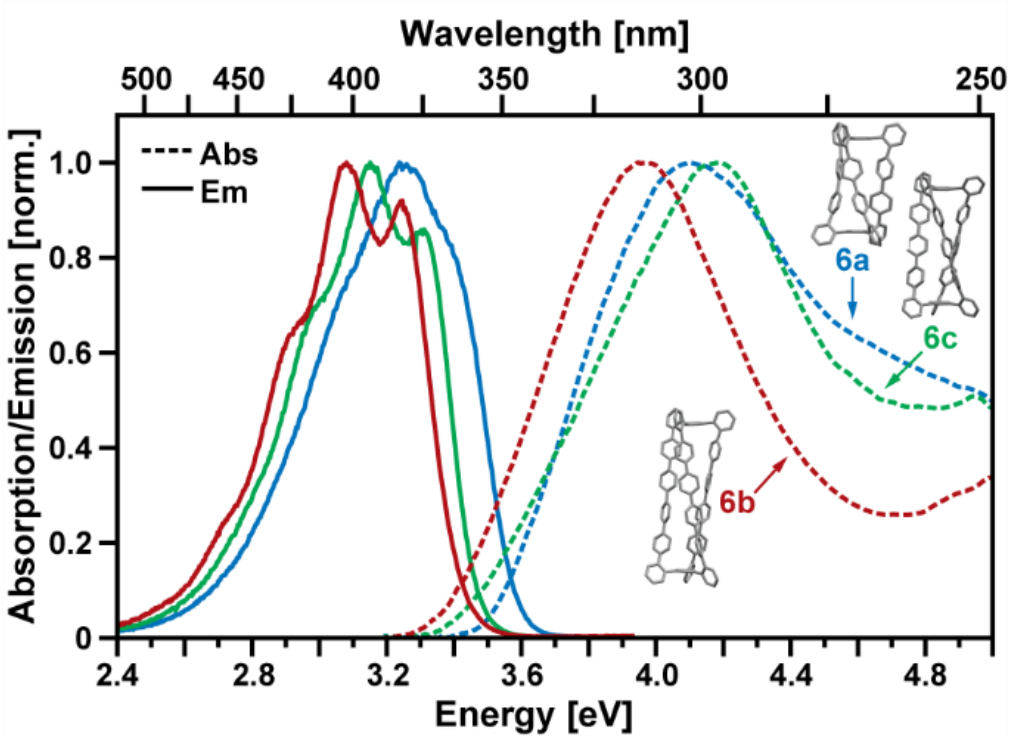


Figure 6.3. Absorption (dashed) & emission spectra (solid, λ_{Ex} = 300 nm) of **6.6a** (blue), **6.6c** (green), and **6.6b** (red) in $CHCl_3$.

interpretation (see experimental detail section). Each emission spectrum has a vibronic progression with a peak spacing of ~1400 cm^{-1} that is attributed to C−C ring stretching, a common feature in spectra of aromatic systems.[22] As the system size is increased, moving from **6.6a** to **6.6c** to **6.6b**, a progressive red-shift of the emission is observed, which suggests extension of the size of the conjugated unit giving rise to emission. Interestingly, this shift is not uniformly reflected in absorption spectra, as the cage of intermediate size **6.6c** displays an absorption maximum that is blue-shifted from the smaller cage **6.6a**. Work examining the physical origin of the observed absorption trend is ongoing.

6.4 Summary

In summary, we have demonstrated a new strategy to prepare oligophenylenes using ruthenium catalyzed diol-diene benzannulation. Subsequently, the tolerance of aryl halides was exploited to achieve the synthesis of novel helical phenylene cages bearing 14, 17, and 20 benzene rings.[23] Those characteristics with X-ray analysis, photophysical and electrophysical measurements, and computational experiments were reported.

6.5 Experimental Details

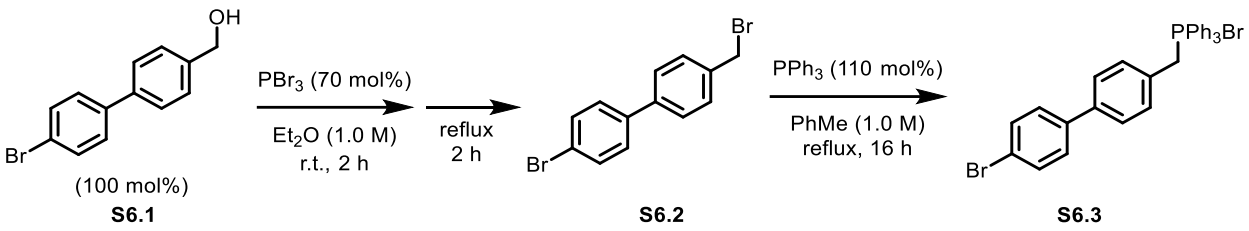
General Comments

All glassware was oven dried at 120 ˚C overnight and cooled in a desiccator. All ruthenium catalyzed reactions were carried out in sealed pressure tubes (13 x 100 mm). THF was purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], dppp, 3,5-dimethylbenzoic acid, $Ni(cod)_2$, 1,10-phenanthroline, CuCN, duqoruinone, ^{t}BuLi were purchased from commercial suppliers and used as received. 1,3,5-tricarbaldehyde **6.1** was prepared according to previous literature.[24] 4-Bromobenzyl triphenylphosphonium bromide was prepared according to previous literature.[25] Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded with a Bruker AVANCE III (500 MHz supported by NSF grant 1 S10 OD021508-01) spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on Agilent Technologies 6530 Accurate-Mass Q-TOF and are reported as m/z. Masses are reported for the molecular ion (M-H, M, M+H or M+Na). MALDI-TOF mass spectra were recorded on a Bruker Autoflex MALDI TOF/TOF Spectrometer using a 337 nm nitrogen laser with tetracyanoquinodimethane (TCNQ) as matrix. Recycling preparative gel permeation

chromatography (GPC) and HPLC separations were carried out on JAI LC-92XXII NEXT using preparative JAIGEL-2HH, 3HH, 2.5HH columns in series with chloroform as eluent.

Synthesis of Starting Materials

Preparation for (4'-bromo-[1,1'-biphenyl]-4-yl)methyl triphenylphosphonium bromide **S6.3**



Benzyl alcohol **S6.1** was synthesized according to known procedures[26] and their characterization data match our own in all respects.

Synthesis of benzyl bromide **S6.2** from benzyl alcohol **S6.1**:

To a solution of **S6.1** (7.9 g, 30.0 mmol, 100 mol%) in anhydrous ether (15 mL) cooled to 0 ˚C was slowly added over 30 minutes phosphorous tribromide (2.0 mL, 21.0 mmol, 70 mol%) in anhydrous ether (15 mL). The mixture was then warmed to room temperature and allowed to stir for 16 hours. The solution was poured into 50 g of ice. The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided the title compound **S6.2** (8.9 g, 27.0 mmol) in 91% yield as a white solid. The product was used to next step without further purification.

TLC (SiO_2): R_f = 0.33 (hexanes : DCM= 90:10).

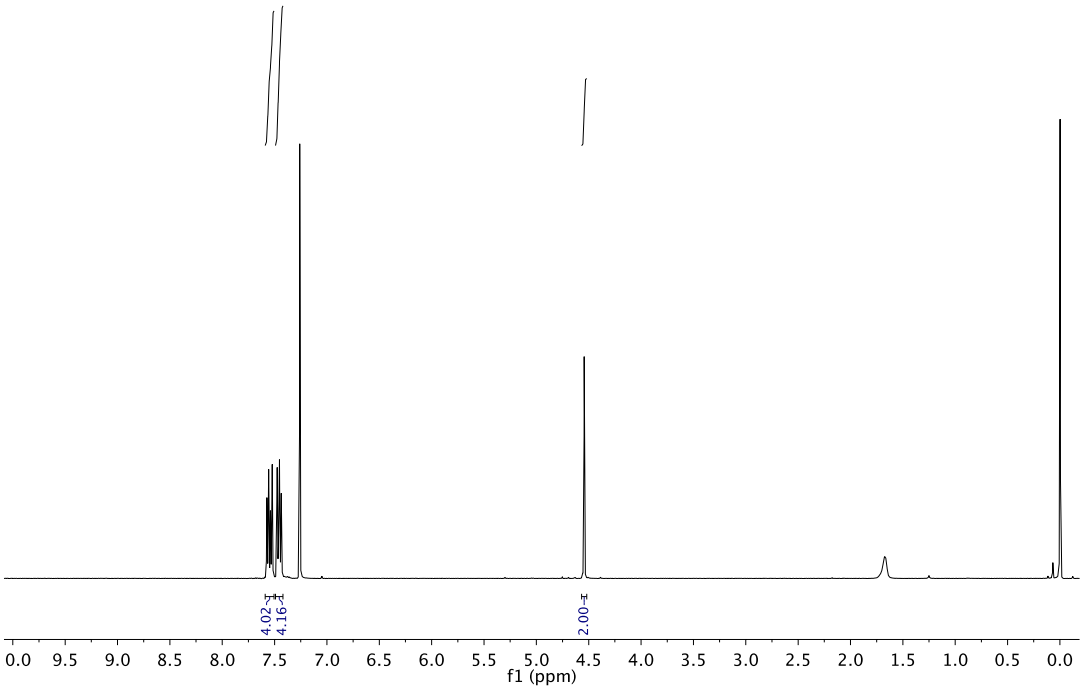
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 17.3 Hz, 2H), 7.54 (d, *J* = 17.0 Hz, 2H), 7.46 (d, *J* = 11.2 Hz, 2H), 7.45 (d, *J* = 11.5 Hz, 2H), 4.54 (s, 2H) ppm.

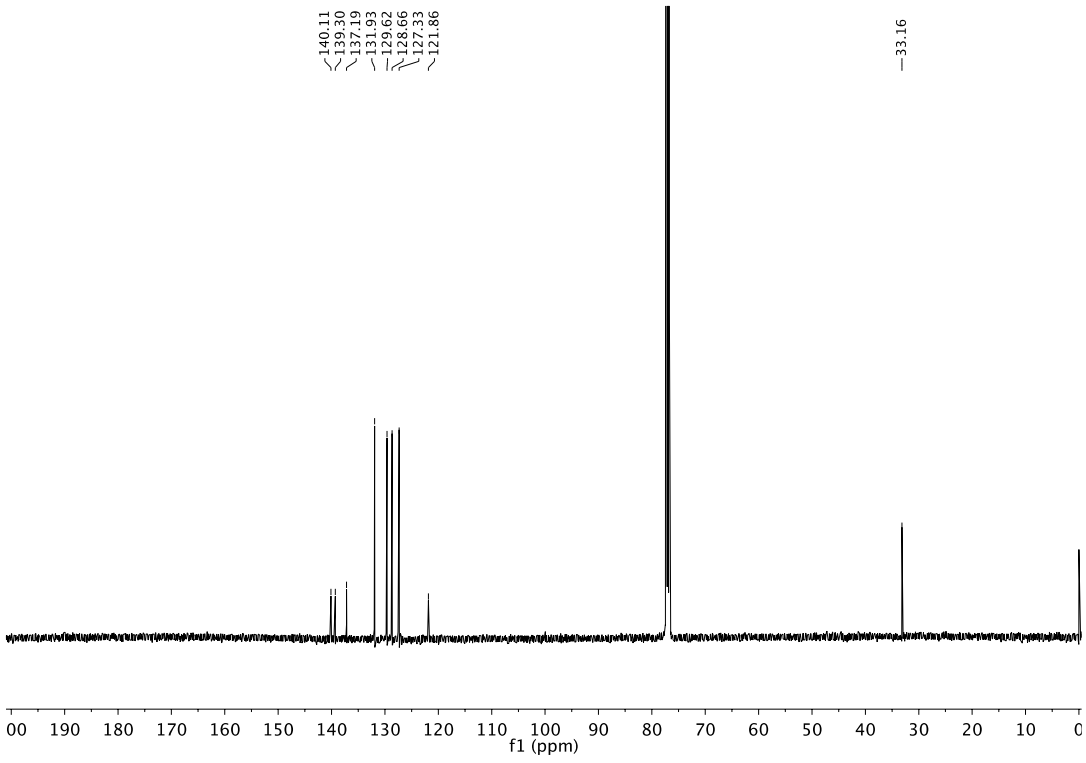
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 140.1, 139.3, 137.2, 131.9, 129.6, 128.7, 127.3, 121.9, 33.2 ppm.

MP: 94-96 ˚C.

HRMS: (CI) Calculated for $C_{13}H_{10}Br_2$ [MH^+] = 326.9207, Found 326.9196.

FTIR: (neat): 1478, 1001, 810 cm^{-1}.


4.02
4.16
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.11
139.30
137.19
131.93
129.62
128.66
127.33
121.86
33.16
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of Wittig reagent **S6.3** from benzyl bromide **S6.2**:

To a solution of **S6.2** (8.9 g, 27.0 mmol, 100 mol%) in toluene (27 mL) was added triphenylphosphine (7.8 g, 29.7 mmol, 110 mol%). The mixture was then refluxed for 16 hours. The solid was filtered under vacuum, and washed with toluene. The title compound **S6.3** (15.2 g, 24.6 mmol) was obtained in 96% yield as a white solid. The product was used to next step without further purification.

TLC (SiO_2): R_f = 0.15 (ethyl acetate : methanol = 80:20).

^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.83–7.75 (m, 9H), 7.67–7.62 (m, 6H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.36–7.28 (m, 4H), 7.20 (dd, *J* = 8.4, 2.6 Hz, 2H), 5.54 (d, *J* = 14.5 Hz, 2H) ppm.

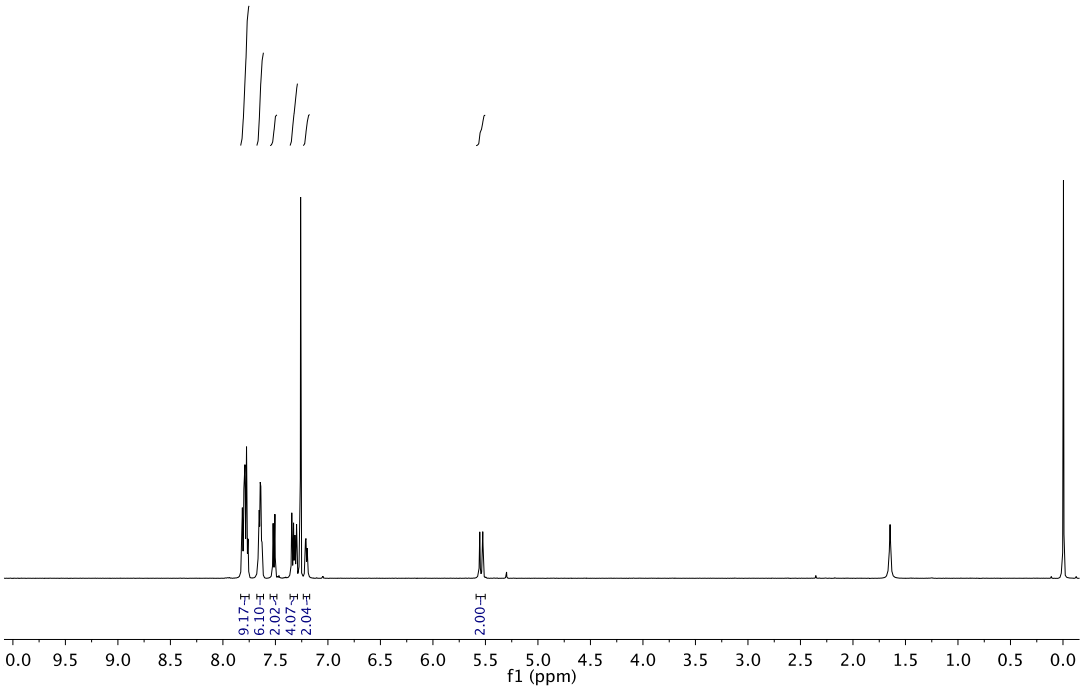
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 139.7, 139.6, 135.0, 134.5 (d), 132.2 (d), 131.9, 130.1 (d), 128.5, 127.0 (d), 126.7 (d), 121.9, 118.0 (d), 30.3 (d) ppm.

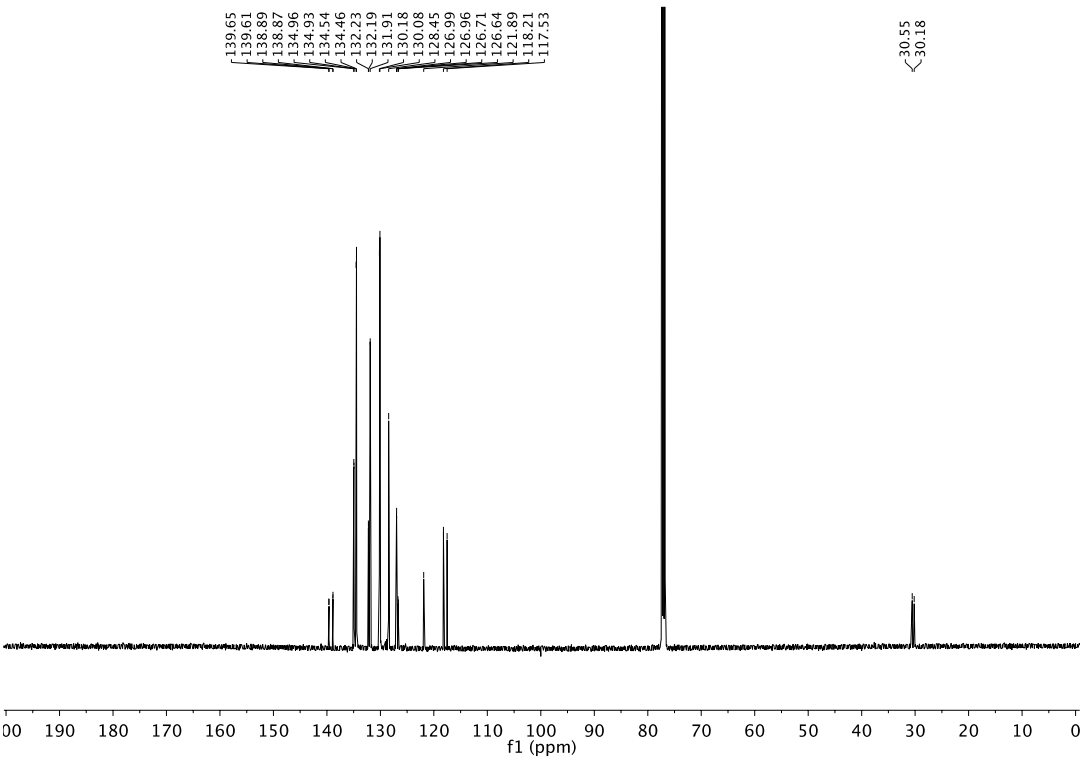
^{31}P NMR: (160 MHz, $CDCl_3$): δ = 22.9 ppm.

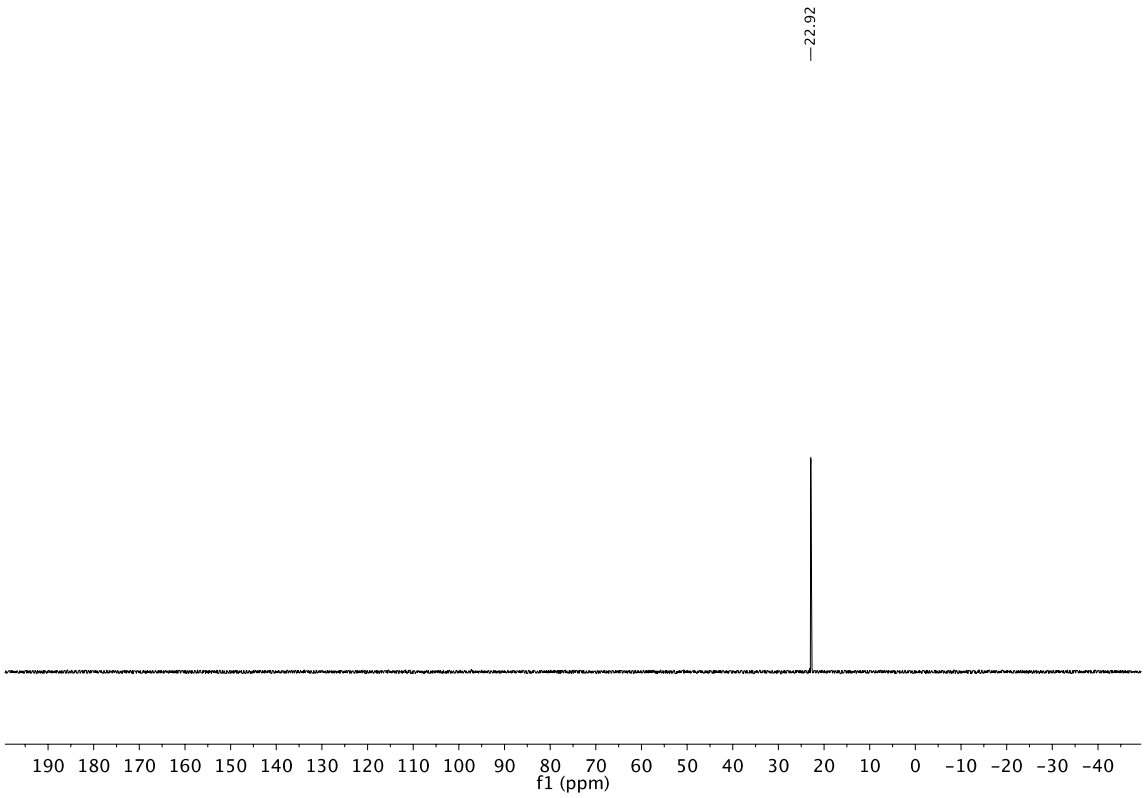
MP: >250 ˚C.

HRMS: (ESI) Calculated for $C_{31}H_{25}BrP$ $[M\text{-}Br]^+$ = 509.0856, Found 509.0855.

FTIR: (neat): 1436, 1109, 837 cm^{-1}.

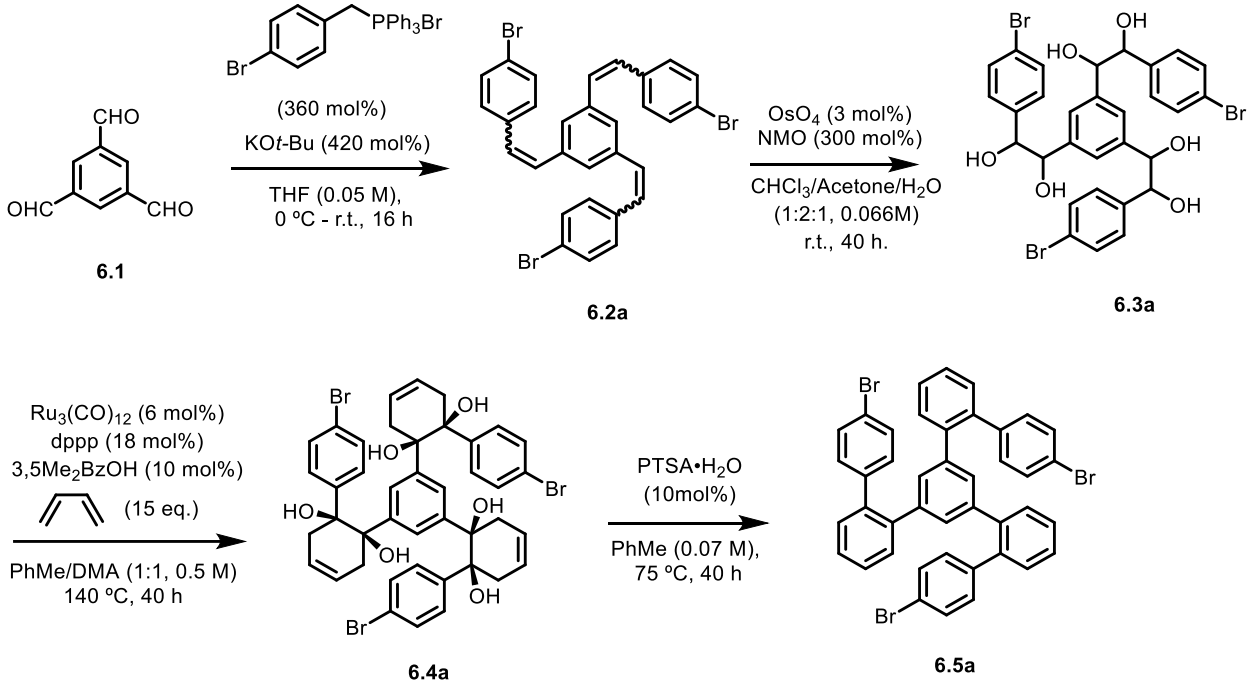

9.17
6.10
2.02
4.07
2.04
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


139.65
139.61
138.89
138.87
134.96
134.93
134.54
134.46
132.23
132.19
131.91
130.18
130.08
128.45
126.99
126.96
126.71
126.64
121.89
118.21
117.53
30.55
30.18
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


22.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

Synthesis of *Tris*-bromide

Synthesis of *tris*-bromide **6.5a**



Synthesis of triene **6.2a** from 1,3,5-tricarbaldehyde **6.1**:

To a solution of KO*t*-Bu (4.72 g, 42.0 mmol, 420 mol%) in anhydrous THF (420 mL) cooled to 0 ˚C was added 4-Bromobenzyl triphenylphosphonium bromide (18.4 g, 36.0 mmol, 360 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of 1,3,5-tricarbaldehyde **6.1** (1.62 g, 10.0 mmol, 100 mol%) in THF (420 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 99:1 to 98:2) to furnish the title compound **6.2a** (4.41 g, 7.1 mmol) in 71% yield as a slightly yellow solid.

TLC (SiO_2): R_f = 0.73 (hexanes : ethyl acetate = 90:10).

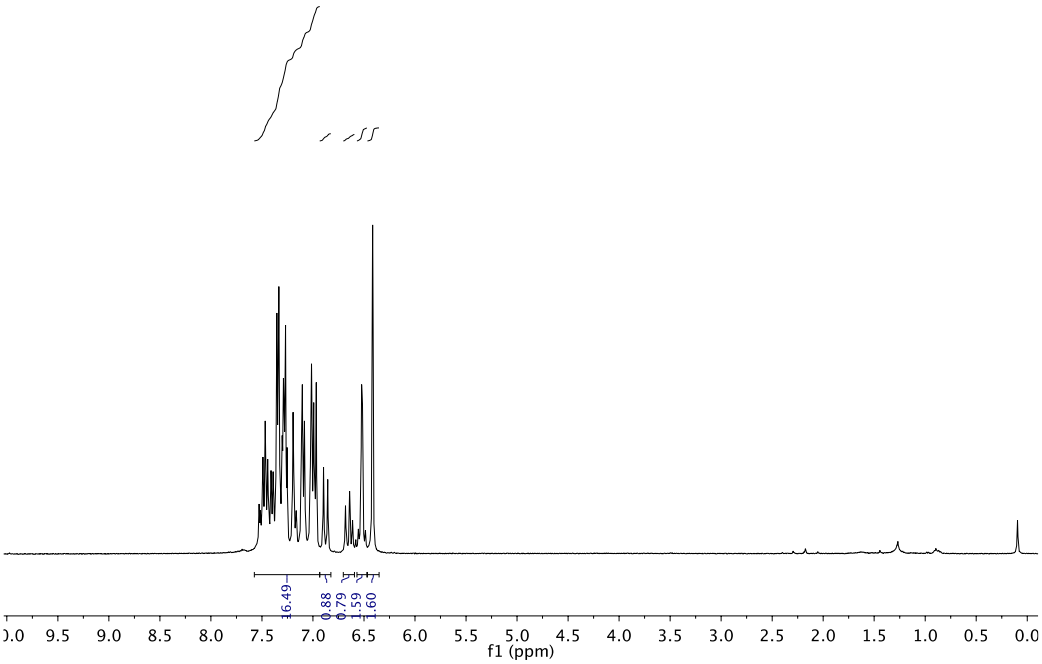
^{1}H NMR: (500 MHz, $CDCl_3$, 3 diastereomers): δ = 7.53–6.86 (m, 17H), 6.66–6.42 (m, 4H) ppm.

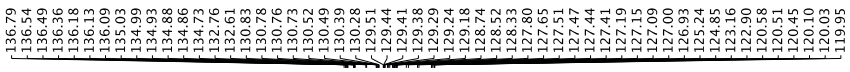
^{13}C NMR: (125 MHz, $CDCl_3$, 3 diastereomers): δ = 136.8, 136.5, 136.5, 136.4, 136.2, 136.1, 136.1, 135.0, 135.0, 134.9, 134.9, 134.9, 134.7, 132.8, 132.6, 120.8, 130.8, 130.8, 130.7, 130.5, 130.5, 130.4, 130.3, 129.5, 129.4, 129.4, 129.4, 129.3, 129.2, 129.2, 128.7, 128.5, 128.3, 127.8, 127.7, 127.5, 127.5, 127.4, 127.4, 127.2, 127.2, 127.1, 127.0, 126.9, 125.2, 124.9, 123.2, 122.9, 120.6, 120.5, 120.5, 120.1, 120.0, 120.0 ppm.

HRMS: (CI) Calculated for $C_{30}H_{21}Br_3$ [M^+] = 621.9173, Found 621.9167.

MP: 129-131 ˚C.

FTIR: (neat): 3012, 2692, 1485, 1071, 1009 cm^{-1}.


16.49
0.88
0.79
1.59
1.60
f1 (ppm)


136.79
136.54
136.49
136.36
136.18
136.13
136.09
135.03
134.99
134.93
134.88
134.86
134.73
132.76
132.61
130.83
130.78
130.76
130.73
130.52
130.49
130.39
130.28
129.51
129.44
129.41
129.38
129.29
129.24
129.18
128.74
128.52
128.33
127.80
127.65
127.51
127.47
127.44
127.41
127.19
127.15
127.09
127.00
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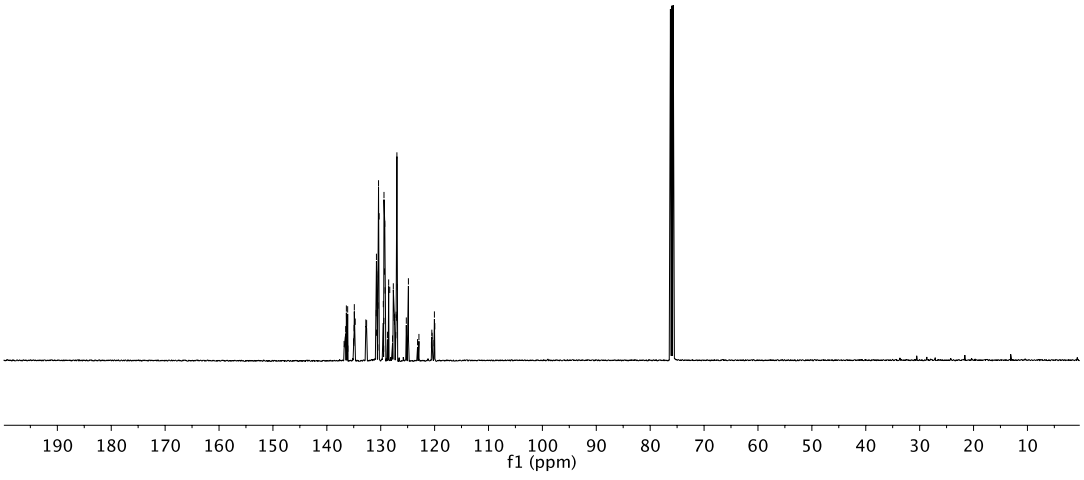
124.85
123.16
122.90
120.58
120.51
120.45
120.10
120.03
119.95


f1 (ppm)

Synthesis of *tris*-diol **6.3a** from triene **6.2a**:

To a solution of triene **6.2a** (3.11 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (3.51 g, 15.0 mmol, 300 mol%). Then, OsO_4 (1.0 M in *t*-BuOH, 0.15 mL, 0.15 mmol, 3 mol%) was added. The mixture was allowed to stir for 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Recovered solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 50:50 to 20:80) to furnish the title compound **6.3a** (1.84 g, 3.5 mmol) in 52% yield as a white solid. The material was characterized by ^{1}H NMR only.

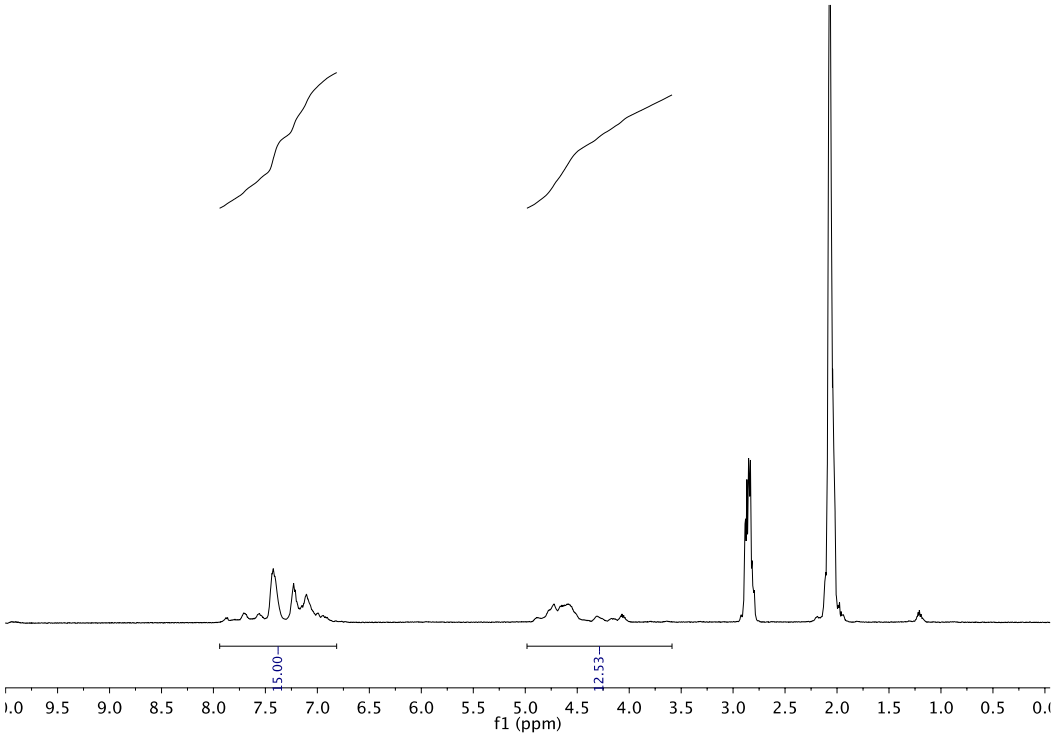
TLC (SiO_2): R_f = 0.42 (ethyl acetate : MeOH = 95:5).

^{1}H NMR: (500 MHz, d_6-acetone, diastereomers): δ = 7.95–6.81 (m, 15H), 4.99–3.59 (m, 12H) ppm.

MP: 121-123 ˚C.

HRMS: (ESI) Calculated for $C_{30}H_{27}Br_3O_6$ [M+Na^+] =744.9231, Found 744.9220.

FTIR: (neat): 2360, 2343, 1070, 1010cm^{-1}.


15.00
12.53
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

Synthesis of cycloadduct **6.4a** from **6.3a** by ruthenium catalyzed cycloaddition reactions

A resealable pressure tube (ca. 13 x 100 mm) was charged with $Ru_3(CO)_{12}$ (10.7 mg, 0.017 mmol, 6 mol%), dppp (20.8 mg, 0.05 mmol, 18 mol%), 3,5-Me_2BzOH (4.1 mg, 0.028 mmol, 10 mol%), *tris*-diol **6.3a** (200 mg, 0.28 mmol, 100 mol%). The pressure tube was purged with argon and toluene/dimethylacetamide (1:1, 0.56 mL) was added via syringe, followed by freshly condensed butadiene (0.37 mL, 4.2 mmol,15.0 eq). The septum was replaced with a screw cap, and the reaction was placed in a 140 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, hexanes:ethyl acetate =80:20 to 45:55) providing the title compound **6.4a** (193 mg, 0.22 mmol) in 81% yield as a slightly yellow solid. The material was characterized by ^{1}H NMR only.

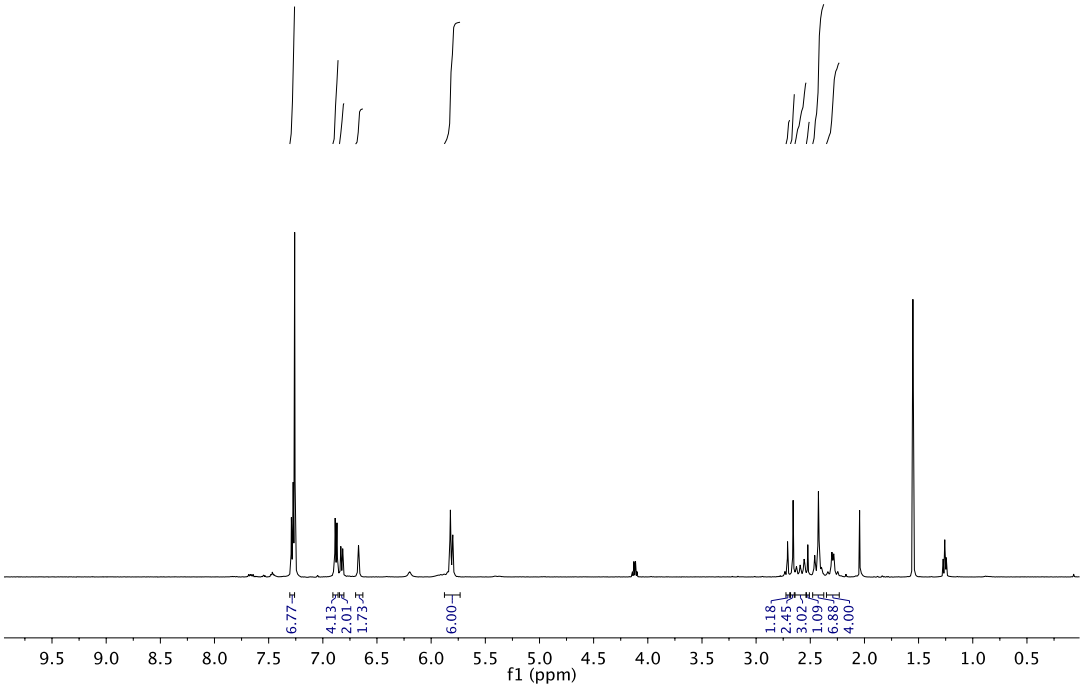
TLC (SiO_2): R_f = 0.20 (hexanes : ethyl acetate = 50:50).

^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.2 Hz, 7H), 6.89–6.82 (m, 6H), 6.67 (s, 2H), 2.71–2.28 (m, 18H) ppm.

MP: decomposed at ~ 180 ˚C.

HRMS: (ESI) Calculated for $C_{42}H_{39}Br_3O_6$ [M+Na^+] = 903.0157, Found 903.0168.

FTIR: (neat): 1738, 1365, 1217 cm^{-1}.


6.77
4.13
2.01
1.73
6.00
1.18
2.45
3.02
1.09
6.88
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

Synthesis of tribromide **6.5a** by dehydration of **6.4a**

A resealable pressure tube (ca. 13 x 100 mm) was charged with cycloadduct **6.4a** (100 mg, 0.11 mmol, 100 mol%) followed by *p*-toluenesulfonic acid monohydrate (2.1 mg, 0.011 mmol, 10 mol%). The pressure tube was purged with argon and toluene (1.6 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in a 75 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The toluene was removed *in vacuo,* and the residue was subjected to flash column chromatography (SiO_2, hexanes:DCM = 90:10) providing the title compound **6.5a** (77.1 mg, 0.10 mmol) in 90% yield as a white solid.

TLC (SiO_2): R_f = 0.28 (hexanes : DCM = 90:10).

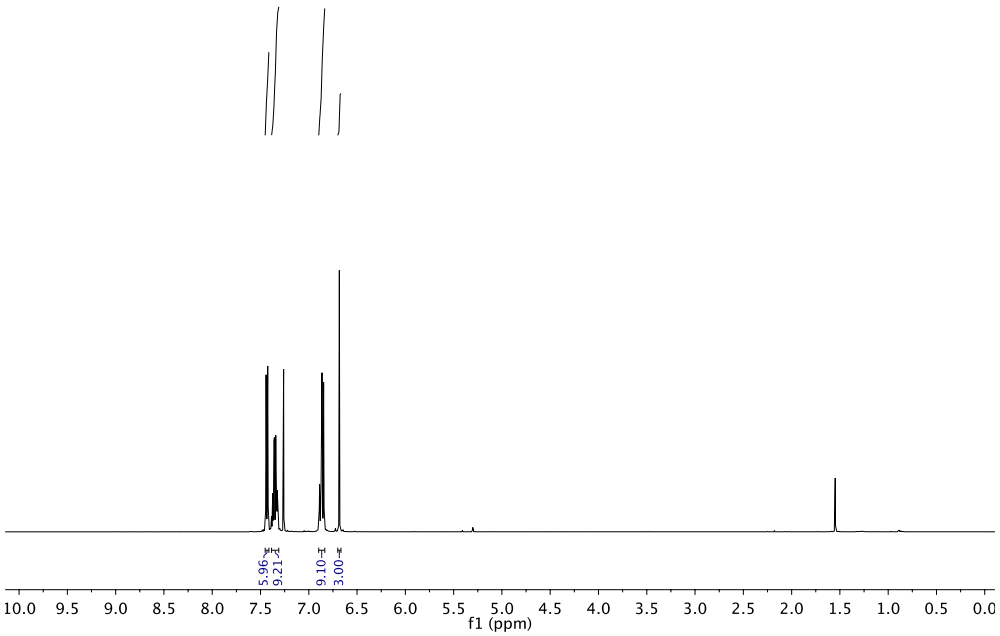
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 6H), 7.38–7.32 (m, 9H), 6.89–6.83 (m, 9H), 6.68 (s, 3H) ppm.

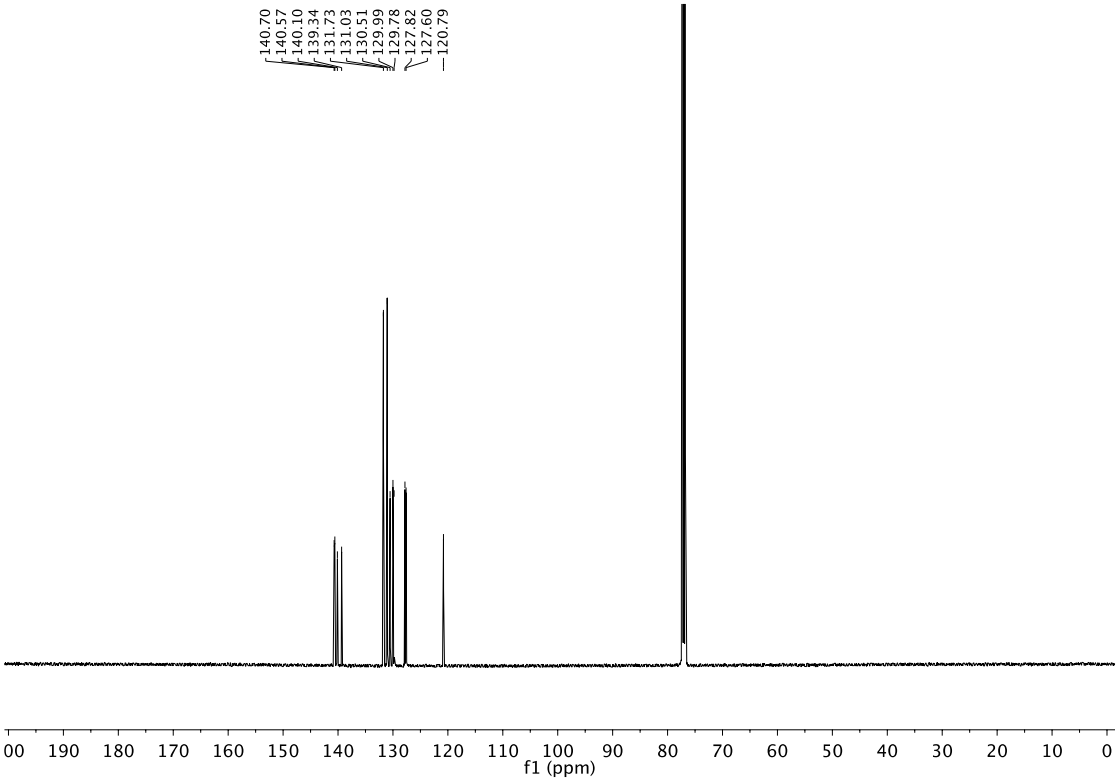
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 140.7. 140.6, 140.1, 139.3, 131.7, 131.0, 130.5, 130.0, 129.8, 127.8, 127.6, 120.8 ppm.

MP: >250 ˚C.

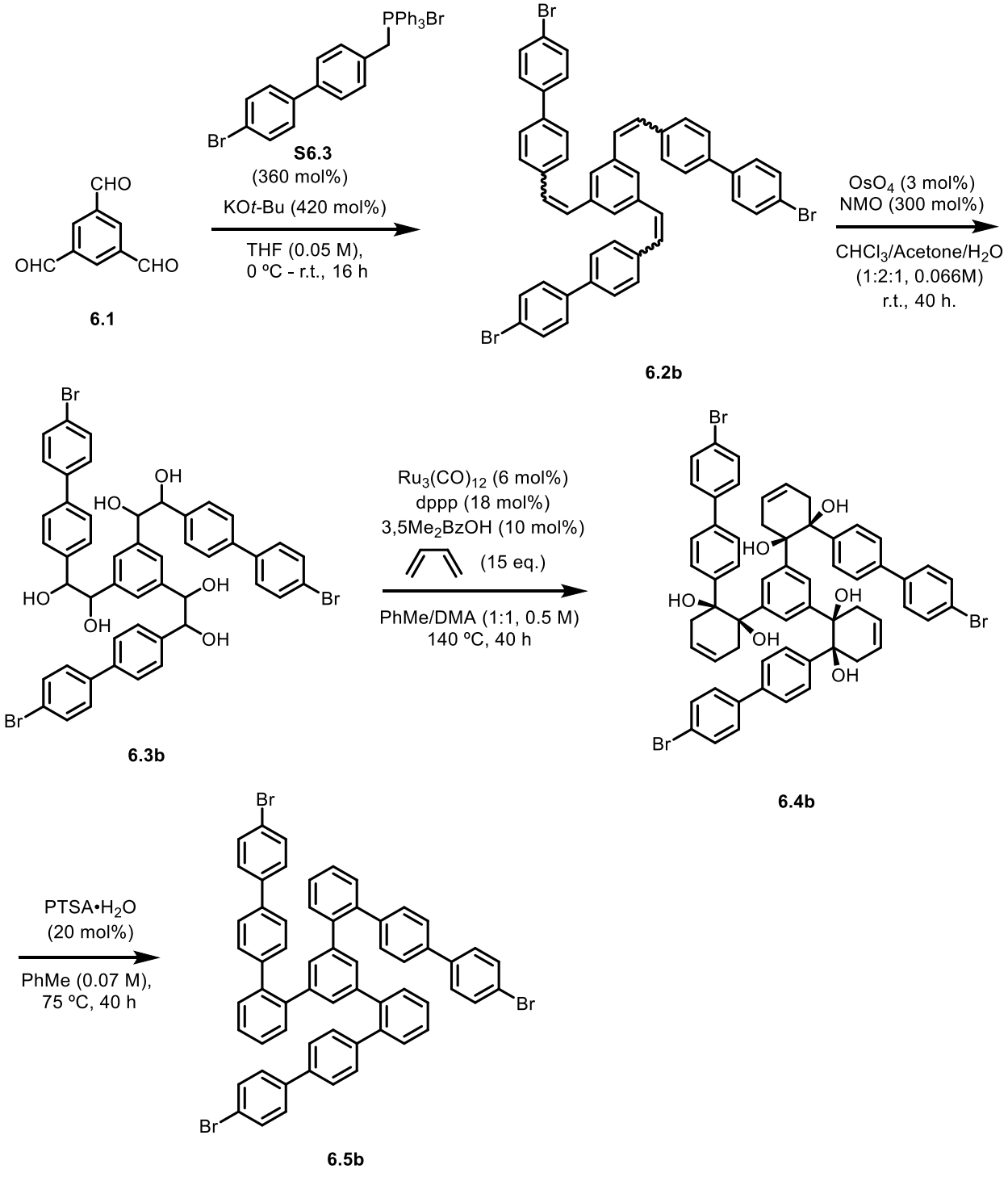
HRMS: (CI) Calculated for $C_{42}H_{27}Br_3$ [M^+] = 769.9642, Found 769.9670.

FTIR: (neat): 2362, 2342, 1739, 1366, 1217 cm^{-1}.


5.96
9.21
9.10
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.70
140.57
140.10
139.34
131.73
131.03
130.51
129.99
129.78
127.82
127.60
120.79
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of *tris*-bromide **5b**



Synthesis of triene **6.2b** from trisaldehyde **6.1**:

To a solution of KO*t*-Bu (3.5 g, 31.5 mmol, 420 mol%) in anhydrous THF (75 mL) cooled to 0 ˚C was added phosphonium salt (8.9 g, 27.0 mmol, 360 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of tricarbonyl **6.1** (1.2 g, 7.5 mmol, 100 mol%) in THF (75 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 99:1 to 98:2) to furnish the title compound **6.2b** (3.6 g, 4.0 mmol) in 57% yield as a white solid.

TLC (SiO_2): R_f = 0.28 (hexanes : DCM = 90:10).

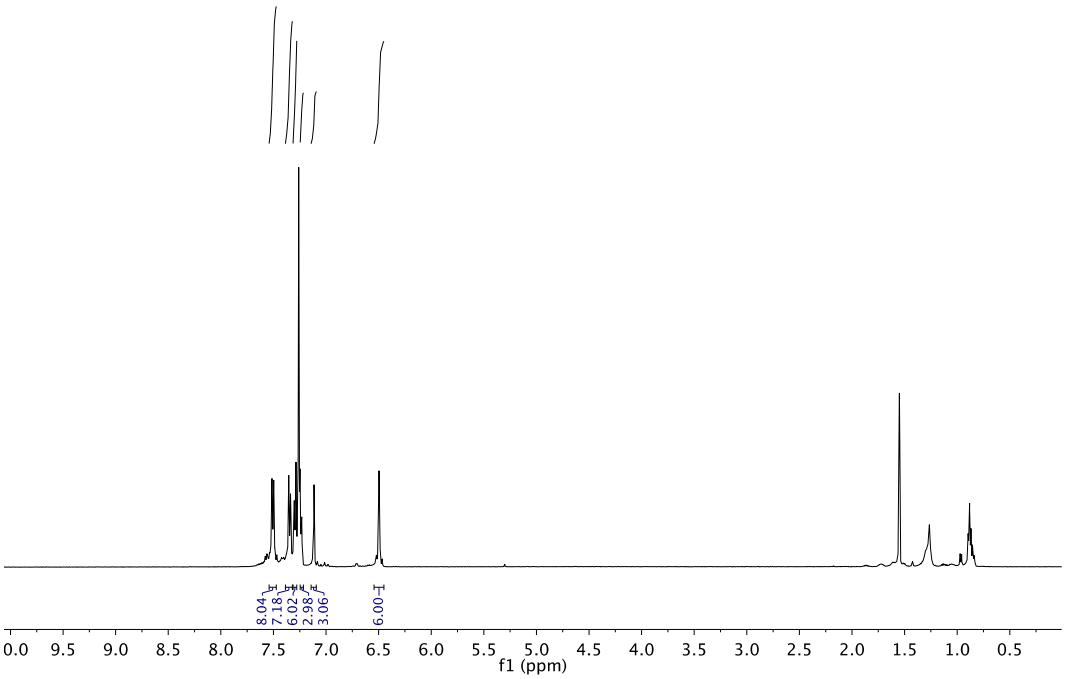
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.54–7.48 (m, 8H), 7.39–7.32 (m, 7H), 7.32–7.28 (m, 6H), 7.26–7.22 (m, 3H), 6.55–6.45 (m, 6H) ppm.

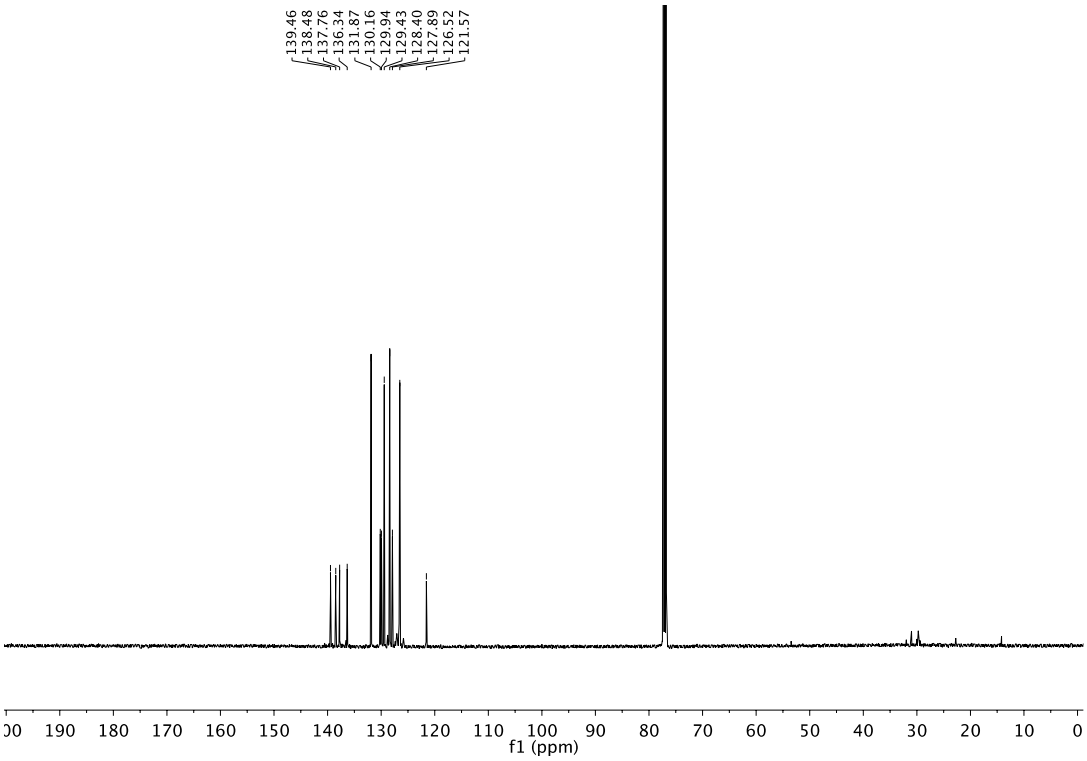
^{13}C NMR: (125 MHz, $CDCl_3$) major diastereomer: δ = 139.5, 138.5, 137.8, 136.3, 131.9, 130.2, 129.9, 129.4, 128.4, 127.9, 126.5, 121.6 ppm.

MP: 180 - 183 ˚C.

HRMS: (ESI) Calculated for $C_{48}H_{33}Br_3$ [MH^+] = 849.0189, Found 849.0200.

FTIR: (neat): 1366, 1229, 1217, 814 cm^{-1}.


8.04
7.18
6.02
2.98
3.06
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


139.46
138.48
137.76
136.34
131.87
130.16
129.94
129.43
128.40
127.89
126.52
121.57
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of *tris*-diol **6.3b** from triene **6.2b**:

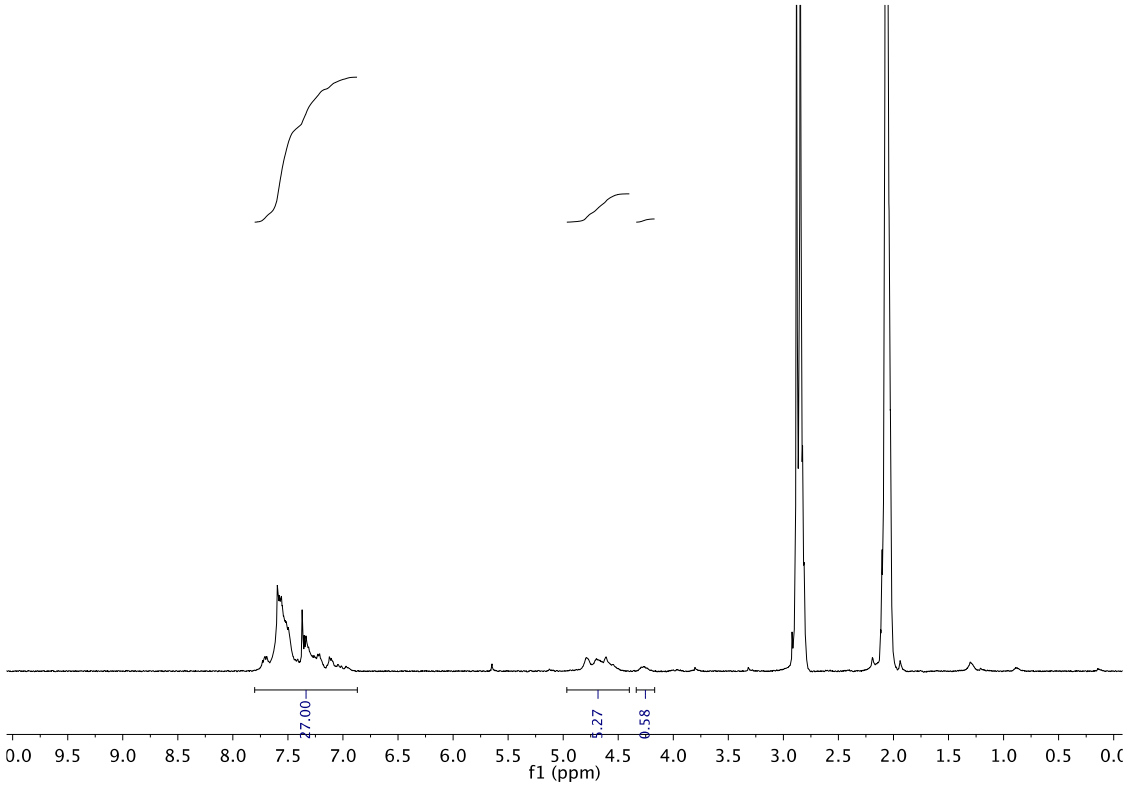
To a solution of triene **6.2b** (3.0 g, 3.5 mmol, 100 mol%) in acetone (27 mL), chloroform (14 mL), and water (13 mL) was added NMO in water (w/w 50%) (2.5 g, 10.5 mmol, 300 mol%). Then, OsO_4 (1.0 M in *t*-BuOH, 105 µL, 0.105 mmol, 3 mol%) was added. The mixture was allowed to stir 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Provided solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 50:50 to 0:100) to furnish the title compound **6.3b** (2.0 g, 2.1 mmol) in 61% yield as a white solid. The material was characterized by ^{1}H NMR only.

TLC (SiO_2): R_f = 0.45 (ethyl acetate : MeOH = 95:5).

^{1}H NMR: (500 MHz, d_6-acetone, mixture of diastereomers): δ = 7.60–6.85 (m, 27H), 4.73–4.15 (m, 6H), 4.06–3.70 (br, 1H), 4.49–4.30 (m, 6H), 3.21 (s, 0.2H), 2.50 (s, 0.3H), 1.99–1.92 (m, 4H), 1.87 (s, 0.5H) ppm.

LRMS: (CI) Calculated for $C_{48}H_{39}Br_3O_6$ [MH^+] = 951.0, Found 951.0.

FTIR: (neat): 3434, 3402, 3390, 2921, 1236, 1043 cm^{-1}.


27.00
5.27
0.58
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Synthesis of cycloadduct **6.4b** from **6.3b** by Ruthenium catalyzed cycloaddition reactions

A resealable pressure tube (ca. 13 x 100 mm) was charged with $Ru_3(CO)_{12}$ (8.0 mg, 0.013 mmol, 6 mol%), dppp (16.1 mg, 0.05 mmol, 18 mol%), 3,5-Me_2BzOH (4.0 mg, 0.021 mmol, 10 mol%), *tris*-diol **6.3b** (200 mg, 0.21 mmol, 100 mol%). The pressure tube was purged with argon and toluene/dimethylacetamide (1:1, 0.42 mL) was added via syringe, followed by freshly condensed butadiene (0.28 mL, 3.2 mmol,15.0 eq). The septum was replaced with a screw cap, and the reaction was placed in a 140 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, hexanes:ethyl acetate =80:20 to 40:60) providing the title compound **6.4b** (209 mg, 0.20 mmol) in 90% yield as a slightly yellow solid. The material was characterized by ^{1}H NMR only.

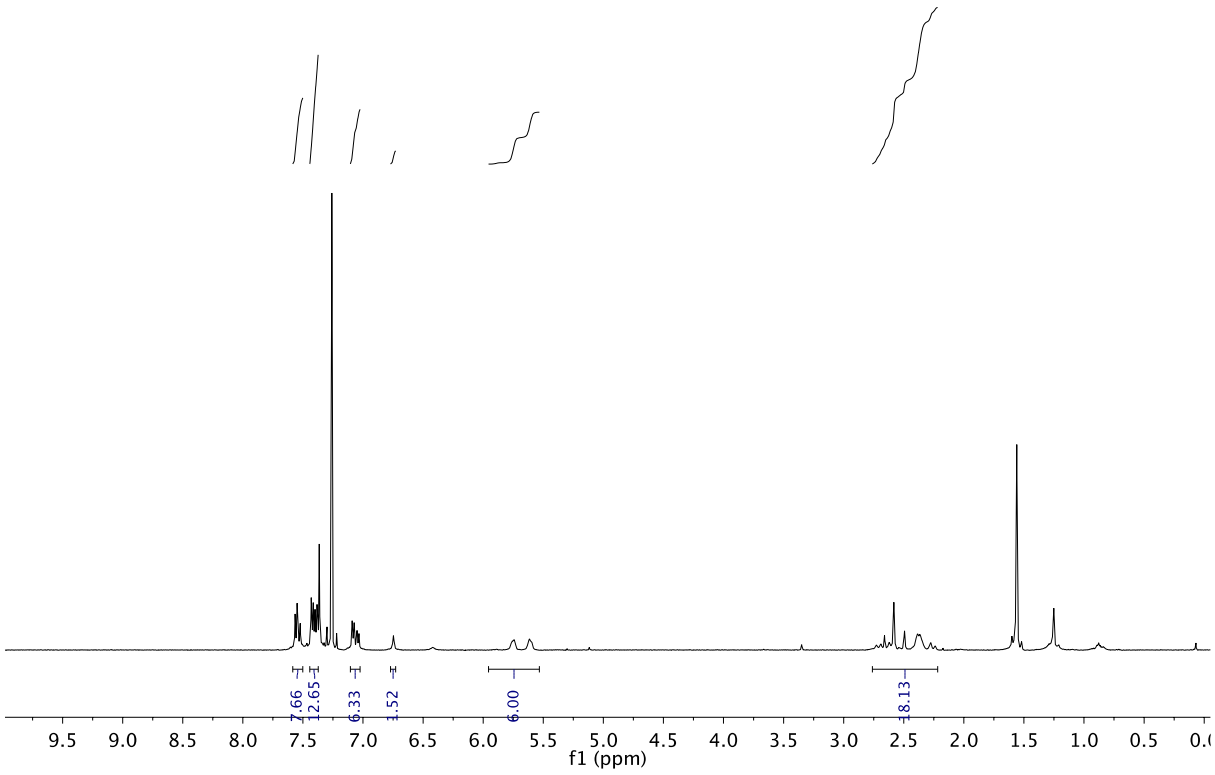
TLC (SiO_2): R_f = 0.58 (hexanes : ethyl acetate = 80:20).

^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.58–7.25 (m, 20H), 7.08–6.66 (m, 7H), 5.87–5.45 (m, 6H), 2.70–2.42 (m, 10H) 2.37–2.14 (m, 8H) ppm.

MP: decomposed at ~190 ˚C.

HRMS: (ESI) Calculated for $C_{60}H_{51}Br_3O_6$ [M+Na^+] = 1131.1104, Found 1131.1127.

FTIR: (neat): 3503, 2923, 1482, 1073, 816 cm^{-1}.


7.66
12.65
6.33
1.52
6.00
18.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

Synthesis of tribromide **6.5b** by Dehydration of **6.4b**

A resealable pressure tube (ca. 13 x 100 mm) was charged with cycloadduct **6.4b** (50 mg, 0.045 mmol, 100 mol%) followed by *p*-toluenesulfonic acid monohydrate (1.7 mg, 0.009 mmol, 20 mol%). The pressure tube was purged with argon and toluene (0.64 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in a 75 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The toluene was removed *in vacuo,* and the residue was subjected to flash column chromatography (SiO_2, hexanes:DCM = 90:10 to 80:20) providing the title compound **6.5b** (19.0 mg, 0.019 mmol) in 42% yield as a white solid.

TLC (SiO_2): R_f = 0.55 (hexanes : DCM = 70:30).

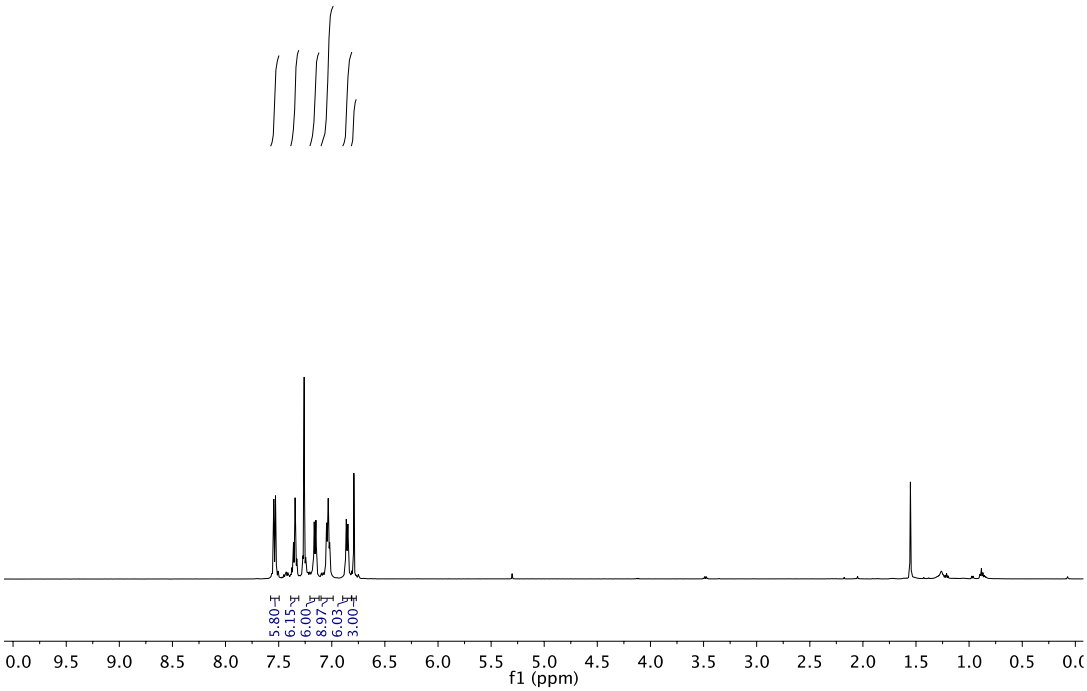
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.5 Hz, 6H), 7.37–7.32 (m, 6H), 7.26–7.22 (m, 3H),7.17 (d, *J* = 7.8 Hz, 6H), 7.06 (d, *J* = 8.1 Hz, 6H), 7.02 (d, *J* = 7.6 Hz, 3H), 6.87 (d, *J* = 7.8 Hz, 6H), 6.79 (s, 3H) ppm.

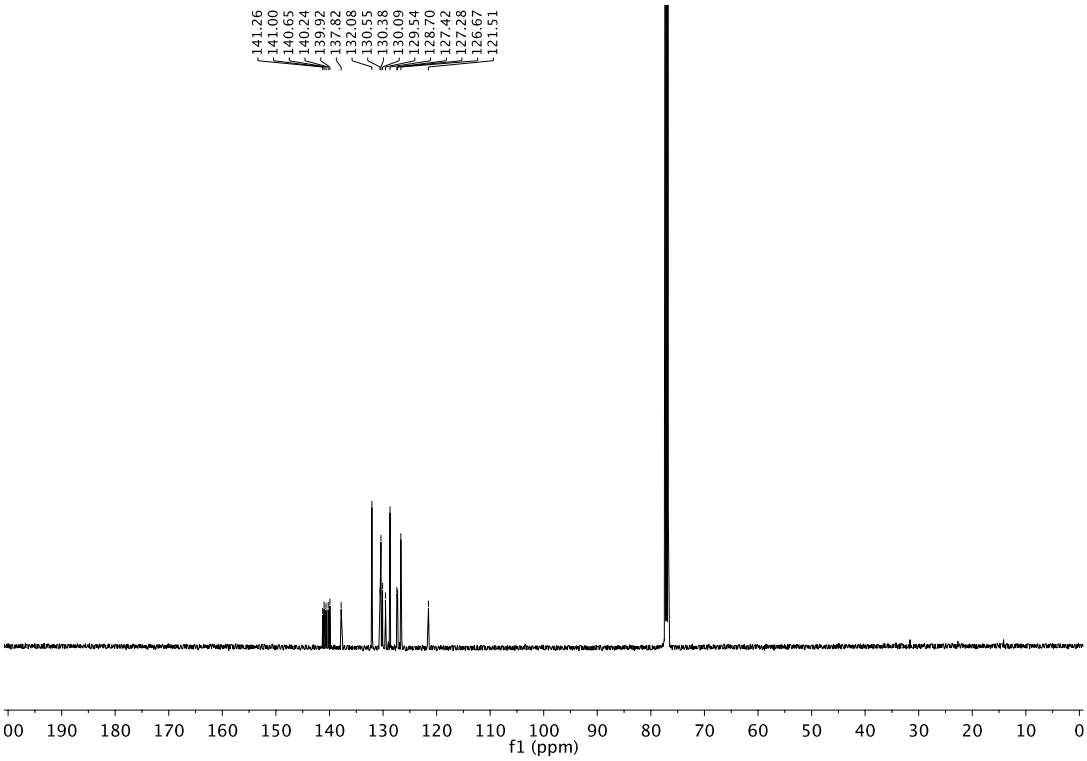
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 141.3, 141.0, 140.7, 140.2, 139.9, 137.8, 132.1, 130.6, 130.4, 130.1, 129.6, 128.7, 127.4, 127.3, 126.7, 121.5 ppm.

MP: >250 ˚C.

HRMS: (ESI) Calculated for $C_{60}H_{39}Br_3$ [M+Na^+] = 1023.0479, Found 1023.0411.

FTIR: (neat): 1365, 1217 cm^{-1}.


5.80
6.15
6.00
8.97
6.03
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


141.26
141.00
140.65
140.24
139.92
137.82
132.08
130.55
130.38
130.09
129.54
128.70
127.42
127.28
126.67
121.51
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of Helical Rod-Like Phenylene Cages

Synthesis of small phenylene cage **6.6a**

A resealable pressure tube was charged with *tris*-bromide **6.5a** (50 mg, 0.065 mmol, 100 mol%). The pressure tube was purged with argon and diethyl ether (3.8 mL) was added via syringe. The reaction mixture was cooled down to -78 ˚C. Then, ^{t}BuLi (1.7 M in pentane, 0.13 mL, 0.20 mmol, 330 mol%) was slowly added. The septum was replaced with a screw cap, and the reaction was stirred for 30 minutes at the same temperature. CuCN (8.7 mg, 0.098 mmol, 150 mol%) was added, and slowly warmed up to ambient temperature over 2 hours. Then, duroquinone (48.0 mg, 0.29 mmol, 450 mol%) was added. After 16 hours, aqueous NH_4Cl and DCM was added. Aqueous phase was extracted with 30 mL DCM three times. The combined organic phases were washed with brine, and dried (Na_2SO_4). The DCM was removed *in vacuo,* and the residue was subjected to flash column chromatography (SiO_2, hexanes:DCM = 95:5 to 85:15) providing the title compound **6.6a** (20.0 mg, 0.019 mmol) in 58% yield as a white solid.

TLC (SiO_2): R_f = 0.28 (hexanes : DCM = 80:20).

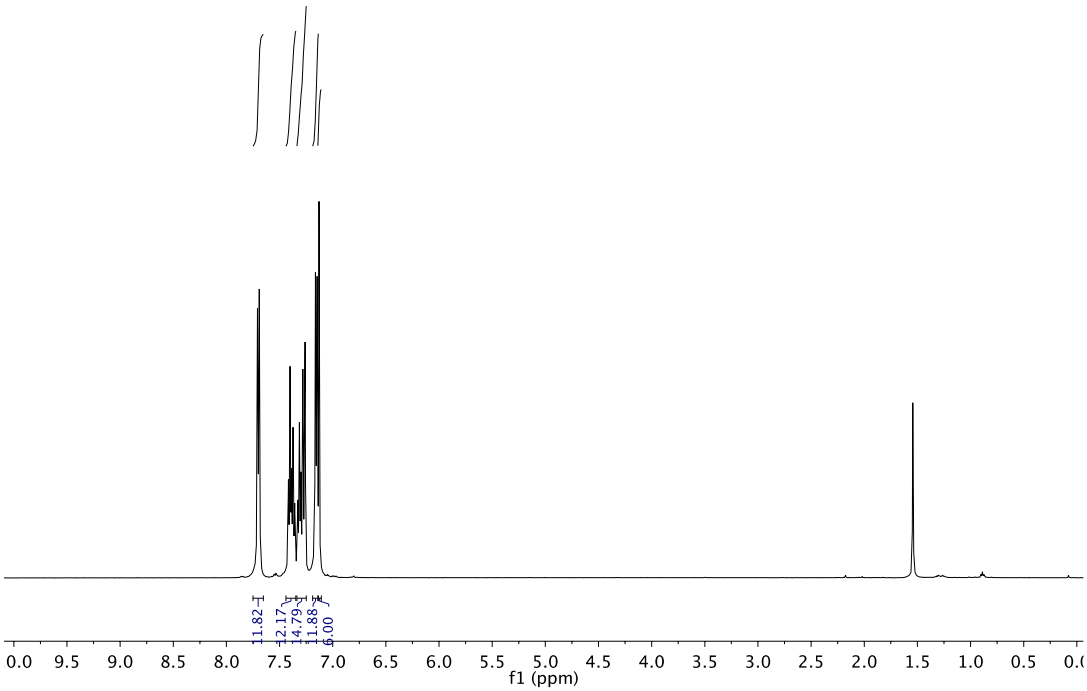
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.0 Hz, 12H), 7.44–7.36 (m, 12H), 7.34–7.25 (m, 12H), 7.15 (d, *J* = 7.9 Hz, 12H) ppm.

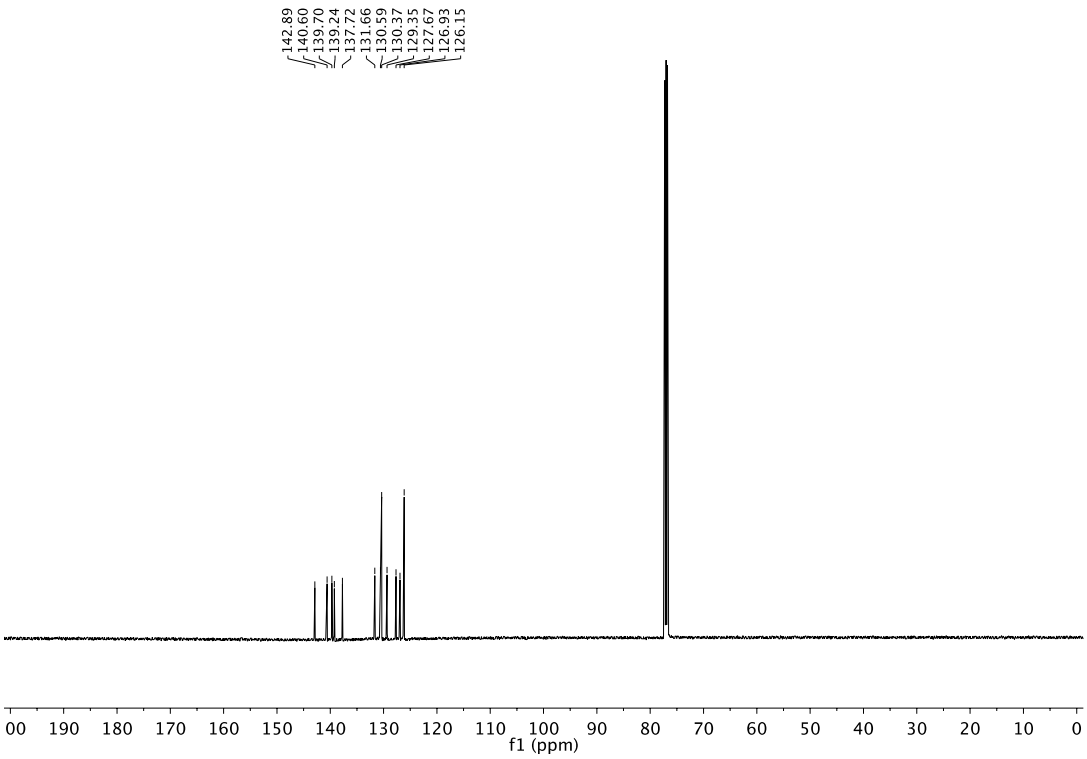
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 142.9, 140.6, 139.7, 139.2, 137.7, 131.7, 130.6, 130.4, 129.4, 127.7, 126.9, 126.2.

MP: >250 ˚C.

FTIR: (neat): 1242, 1177, 1031, 671 cm^{-1}.

HR MALDI-TOF: (TCNQ as a matrix) Calculated for $C_{84}H_{54}$ = 1062.423, Found 1062.423.


11.82
12.17
14.79
11.88
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


142.89
140.60
139.70
139.24
137.72
131.66
130.59
130.37
129.35
127.67
126.93
126.15
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of large phenylene cage **6.6b**

By copper-mediated biaryl coupling

A resealable pressure tube was charged with *tris*-bromide **6.5b** (30.0 mg, 0.030 mmol, 100 mol%). The pressure tube was purged with argon and diethyl ether (9.0 mL) was added via syringe. The reaction mixture was sonicated for 10 minutes until all of the *tris*-bromide dissolved. The reaction vessel was cooled down to -78 ˚C. Then, ^{t}BuLi (1.7 M in pentane, 0.23 mL, 0.40 mmol, 13.2 eq) was slowly added. The septum was replaced with a screw cap, and the reaction was stirred for 30 minutes at the same temperature. CuCN (4.1 mg, 0.045 mmol, 150 mol%) was added, and slowly warmed up to ambient temperature over 2 hours. Then, duroquinone (44.3 mg, 0.27 mmol, 900 mol%) was added. After 16 hours, aqueous NH_4Cl and DCM were added. The aqueous phase was extracted with 30 mL DCM three times. The combined organic phases were washed with brine, dried (Na_2SO_4) and passed through celite with DCM. The DCM was removed *in vacuo*, and the residue was subjected to gel permeation chromatography (GPC) provided the title compound **6.6b** (2.1 mg, 0.0027 mmol) in 9% yield as a white solid.

By nickel-mediated biaryl coupling

A resealable pressure tube was charged with $Ni(cod)_2$ (24.8 mg, 0.090 mmol, 300 mol%), 1,10-phenanthroline (16.8 mg, 0.093 mmol, 310 mol%), and *tris*-bromide **6.5b** (30.0 mg, 0.030 mmol, 100 mol%). The pressure tube was purged with argon and tetrahydrofuran (7.5 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in an oil bath at 80 ˚C. After 40 hours, the reaction vessels were removed from the oil bath and allowed to cool to room temperature. Aqueous NH_4Cl and DCM were added, and the aqueous phase was extracted

with 30 mL DCM three times. The combined organic phases were washed with brine, dried (Na_2SO_4) and passed through celite with DCM. The DCM was removed *in vacuo*, and the residue was subjected to gel permeation chromatography (GPC) providing the title compound **6.6b** (3.9 mg, 0.0051 mmol) in 17% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (hexanes : DCM = 70:30).

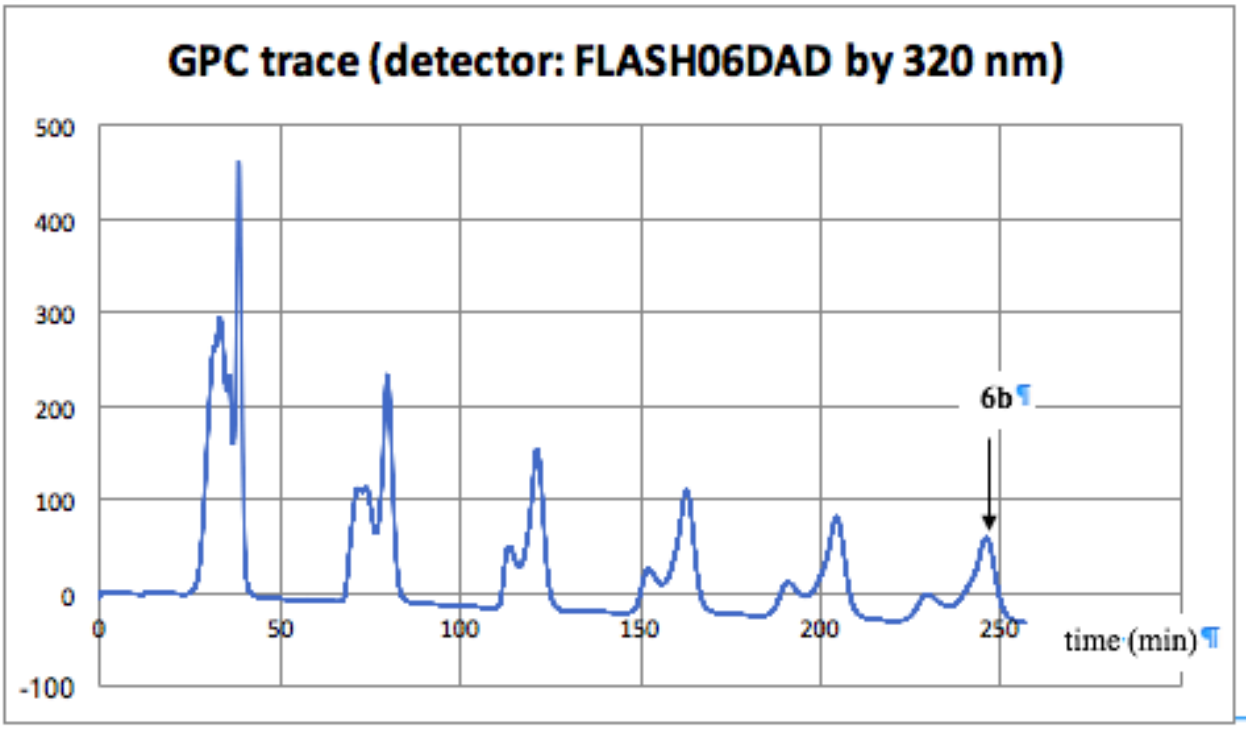
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.41–7.30 (m, 60H), 7.15 (s, 6H), 7.07 (d, *J* = 8.0 Hz, 12H) ppm.

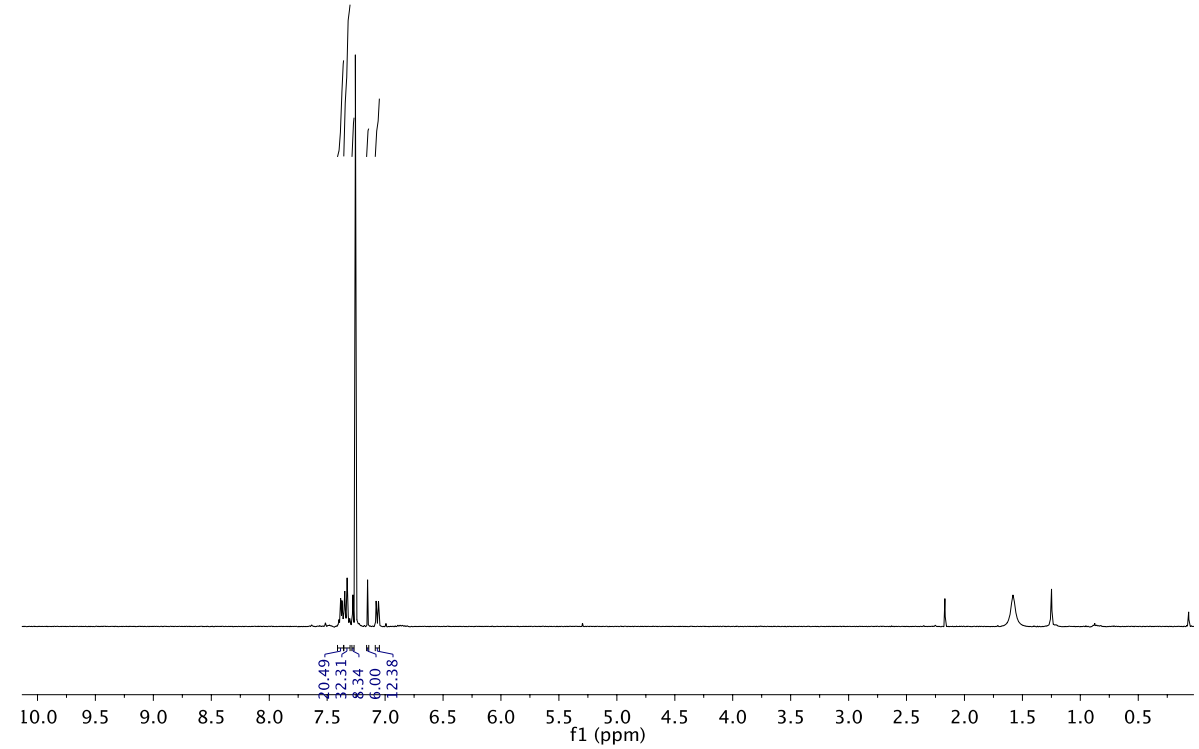
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 142.5, 140.7, 140.1, 139.8, 139.5, 138.7, 138.3, 131.3, 130.6, 130.3, 129.3, 127.6, 127.5, 127.2, 126.8, 126.6.

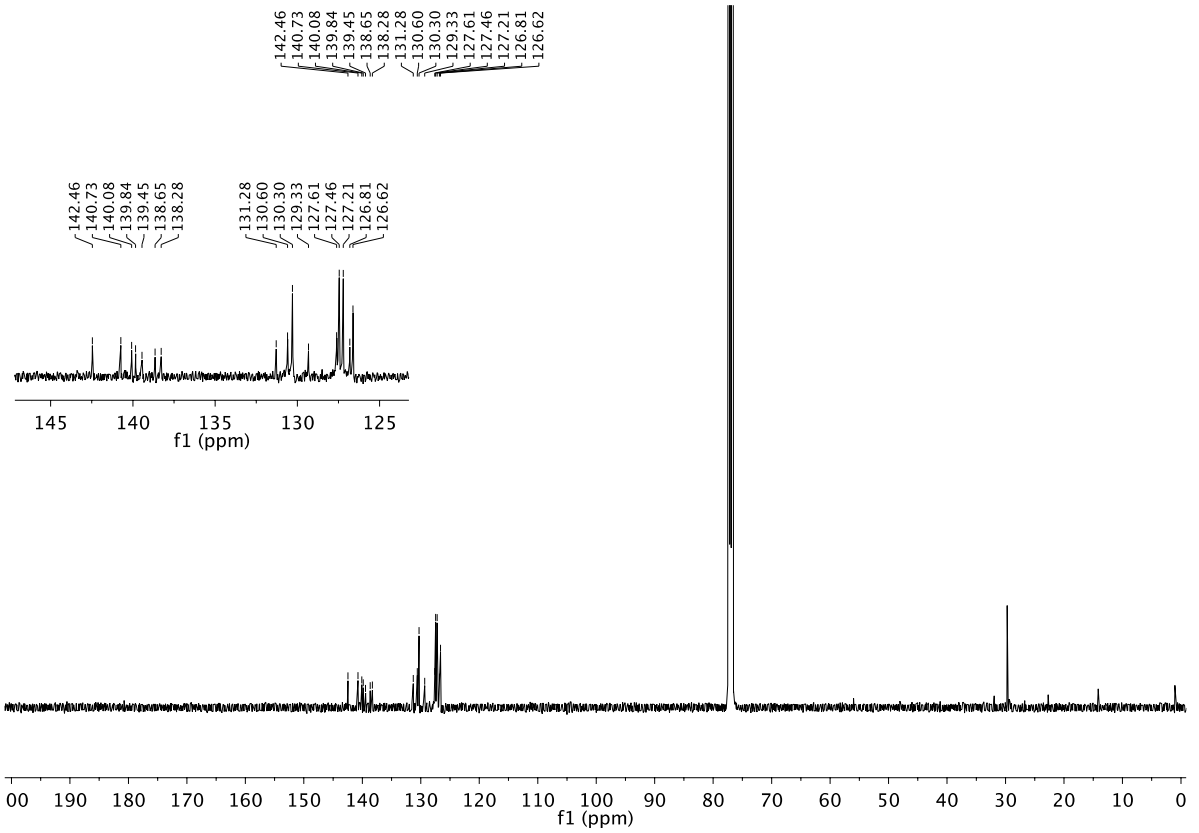
MP: >250 ˚C.

FTIR: (neat): 2113, 1975 cm^{-1}.

HR MALDI-TOF: (TCNQ as a matrix) Calculated for $C_{120}H_{78}$ = 1519.613, Found 1519.613.




20.49
32.31
8.34
6.00
12.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


142.46
140.73
140.08
139.84
139.45
138.65
138.28
131.28
130.60
130.30
129.33
127.61
127.46
127.21
126.81
126.62
145 140 135 130 125
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of medium phenylene cage **6.6c**

A resealable pressure tube was charged with $Ni(cod)_2$ (24.8 mg, 0.090 mmol, 300 mol%), 1,10-phenanthroline (16.8 mg, 0.093 mmol, 310 mol%), *tris*-bromide **6.5a** (23.1 mg, 0.030 mmol, 50 mol%), and *tris*-bromide **6.5b** (30.0 mg, 0.030 mmol, 50 mol%). The pressure tube was purged with argon and tetrahydrofuran (7.5 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in an oil bath at 80 ˚C. After 40 hours, the reaction vessels were removed from the oil bath and allowed to cool to room temperature. The aqueous NH_4Cl and DCM were added, and the aqueous phase was extracted with 30 mL DCM three times. The combined organic phases were washed with brine, dried (Na_2SO_4) and passed through celite with DCM. The DCM was removed *in vacuo,* and the residue was subjected to gel permeation chromatography (GPC) providing **6.6a** (1.3 mg, 0.0012 mmol) in 8% yield, **6.6b** (2.0 mg, 0.0013 mmol) in 9% yield, and **6.6c** (4.6 mg, 0.0036 mmol) in 12% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (hexanes : DCM = 70:30).

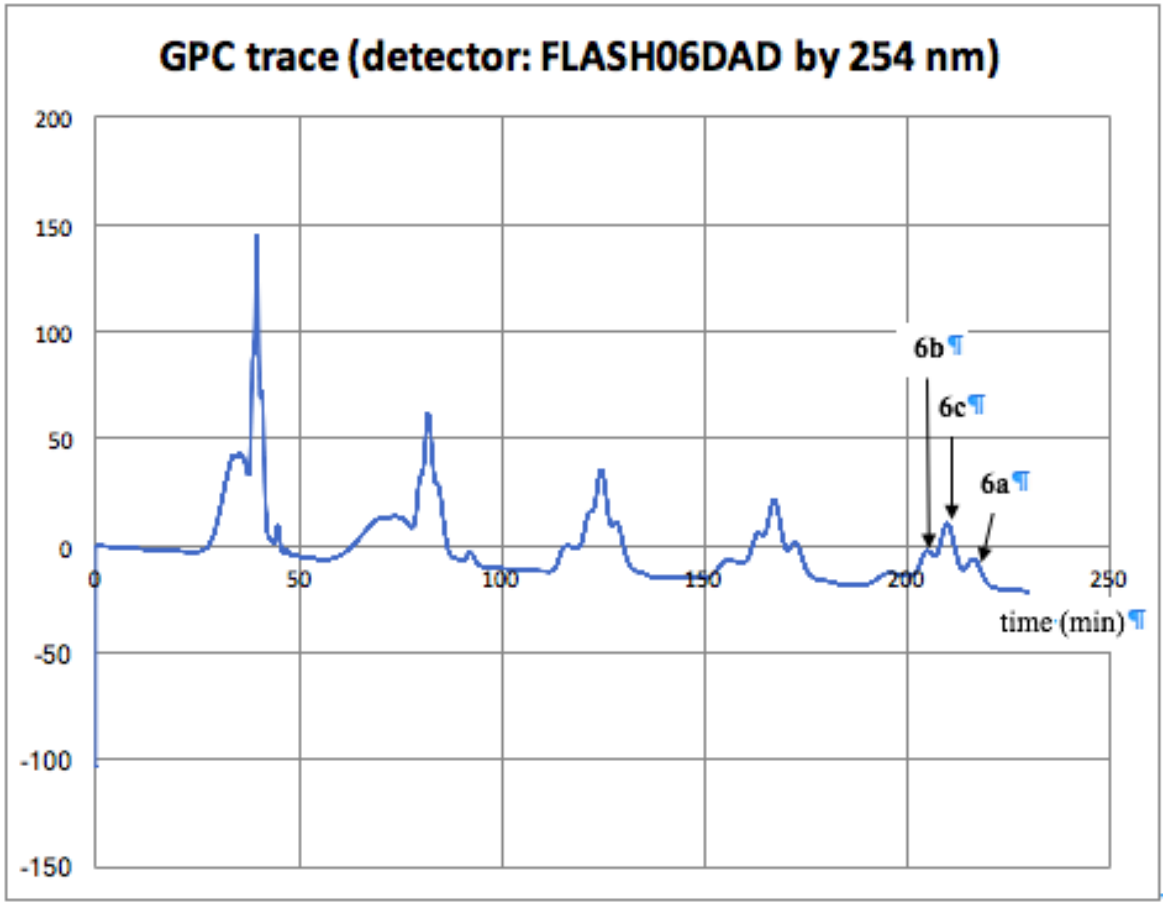
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.43–7.31 (m, 42H), 7.27 (overlapped with $CHCl_3$) (m, 6H), 7.17 (s, 6H), 7.13 (d, *J* = 7.9 Hz, 12H) ppm.

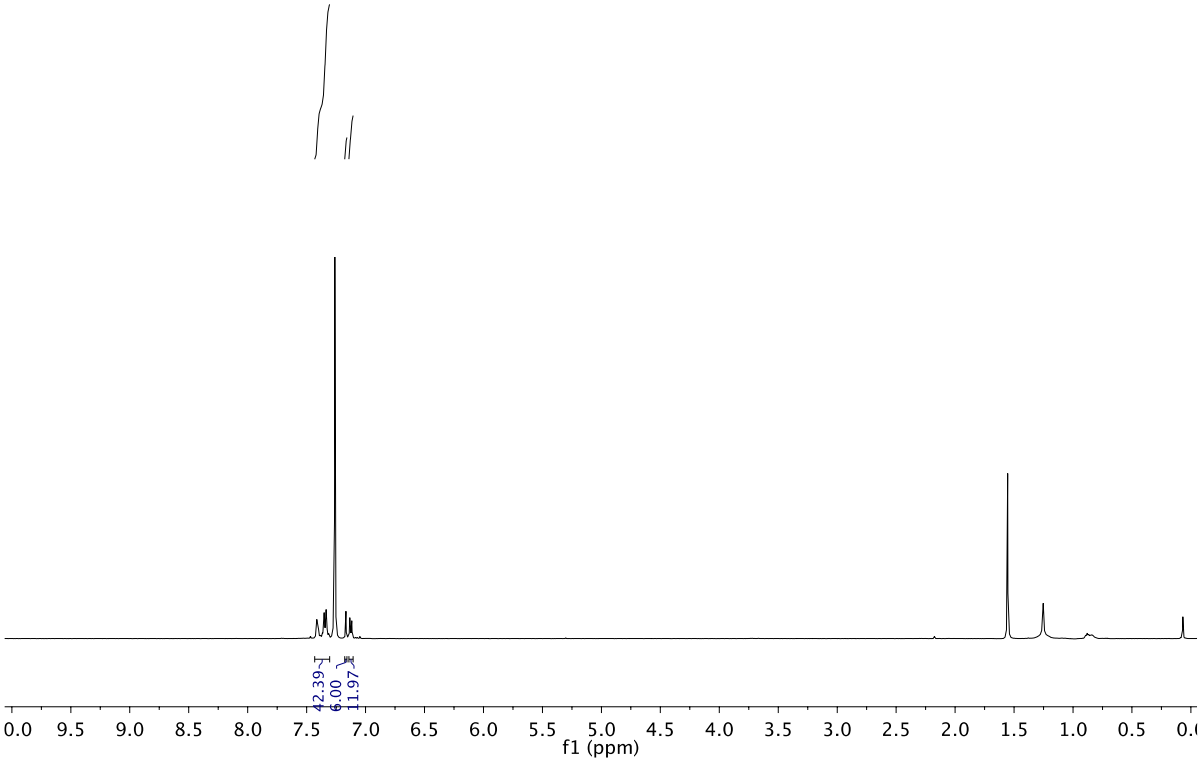
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 142.3, 140.7, 139.9, 139.7, 139.4, 138.4, 131.4, 130.6, 130.3, 129.5, 127.7, 127.5, 126.9, 126.7 ppm.

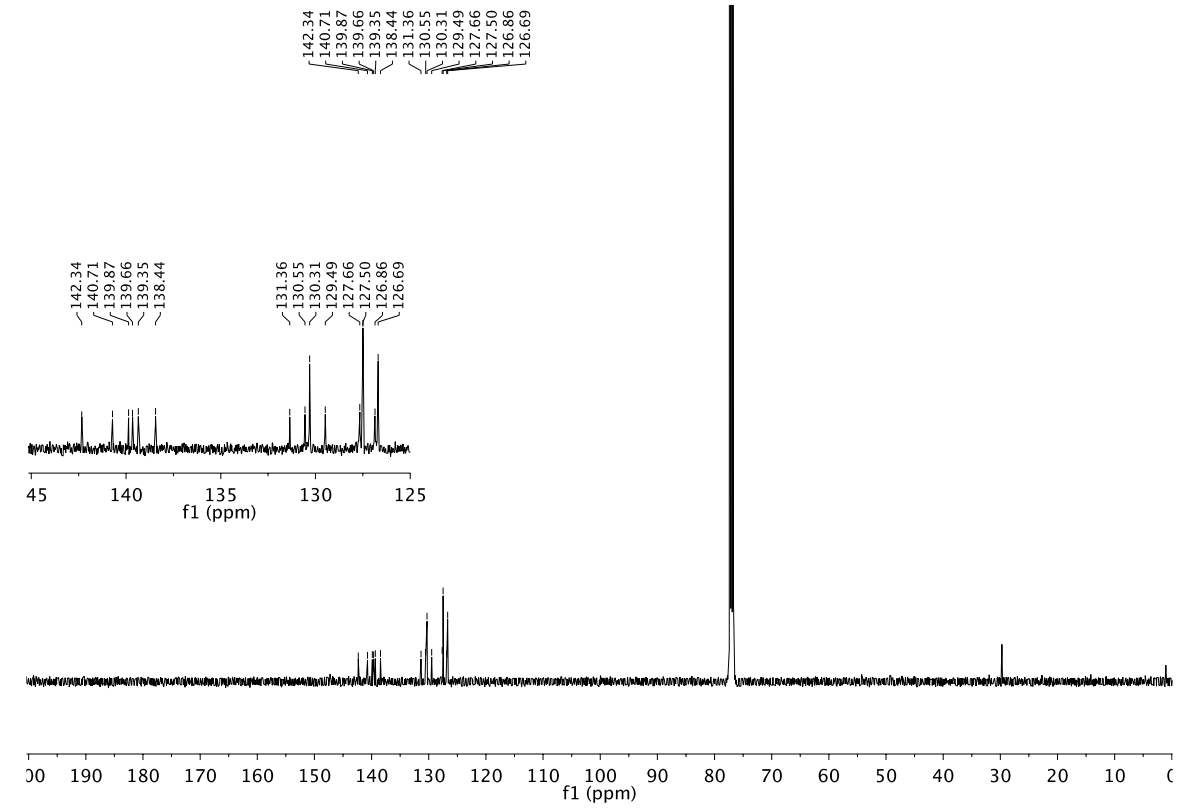
MP: >250 ˚C.

FTIR: (neat): 1632, 759 cm^{-1}.

HR MALDI-TOF: (TCNQ as a matrix) Calculated for $C_{102}H_{66}$ = 1291.516, Found 1291.515.


GPC trace (detector: FLASH06DAD by 254 nm)
200
150
100
50
0
-50
-100
-150
0
50
100
150
200
250
6b
6c
6a
time (min)


42.39
6.00
11.97
f1 (ppm)


142.34
140.71
139.87
139.66
139.35
138.44
131.36
130.55
130.31
129.49
127.66
127.50
126.86
126.69
f1 (ppm)

Spectroscopic Studies

Absorption spectra of **6.6a**, **6.6b** and **6.6c** dissolved in chloroform were obtained from transmittance spectra of dilute solutions in 1 cm pathlength cuvettes measured with a Shimadzu UV-2600 UV-Vis spectrometer using an integrating sphere attachment. Corresponding emission spectra were measured with a Horiba Jobin Yvon Fluorolog3 Fluorimeter on the same samples within the hour exciting at 300 nm in a right angle excitation-collection geometry. Aggregation in the samples used for spectroscopic studies was ruled out by measuring the transmittance of the samples after successive dilutions over orders of magnitude in concentration with no observed changes in absorption profile.

Computational Studies

Structural optimization via DFT was achieved with the Gaussian 09 program.[27] While, DFT single-point calculations at the optimized geometries and TDDFT computations were performed with the NWChem quantum chemistry package.[28] The B3LYP functional and Pople's 6-31G* basis set were used in structural optimization, single-point calculations, and TDDFT calculations.[29] The optimized geometries (Table S2) possessed no imaginary vibrational modes, indicating they are true stationary points on their respective potential energy surfaces. The energies of the molecular orbitals were obtained with a single-point calculation at the optimized geometries. Single-point energies for each molecule are shown in Table S1. With the optimized geometries and DFT results in hand, the first 15 spin-singlet excitations of each molecule were determined via TDDFT within the Tamm-Dancoff approximation.[30] Visualization of frontier molecular orbitals of the small cage (**6.6a**) along the z-axis in Figure S1 was performed in VESTA,[31] and suggests these orbitals experience some degree of delocalization among **6.6a**'s *p*-phenylene chains. The HOMOs of the medium and large phenylene cages are -5.4339 eV and -5.3296 eV, respectively. Their respective LUMOs are -1.2515 eV and -1.3740 eV. As such, we observe a systematic decrease in the HOMO-LUMO energy gap moving from the small to large phenylene cage as is observed for isolated p-phenylene oligomers.

Briefly, TDDFT results indicate the lowest energy spin-singlet excited state (S_1) for the small, medium, and large cages carry negligible oscillator strength with respective energies of 3.9403 eV, 3.6561 eV, and 3.4584 eV. The three excited states with the largest oscillator strength of **6.6a** are 4.0044 eV (S_4), 4.2012 eV (S_9), and 4.2955 eV (S_{10}). For **6.6c**, 3.6633 eV (S_2), 3.8026 eV (S_7), and 3.9478 eV (S_9). Additionally, for the case of **6.6b**, we have 3.5197 eV (S_3), 3.7095

eV (S_8), and 3.7756 eV (S_9). These transitions generally capture the trends observed apart from the blue shift observed between the absorbance maxima moving from the small (**6.6a**) to medium (**6.6c**) phenylene cage. More computational work is underway to describe the system in more detail and subsequently increase our understanding of their unique electronic structure and optical properties.

Table 6.1. Single-point energies (Hartree)

Small Cage **(6.6a)**	Medium Cage **(6.6c)**	Large Cage **(6.6b)**
-2855.771505811825	-3467.857531177830	-4079.961098984862

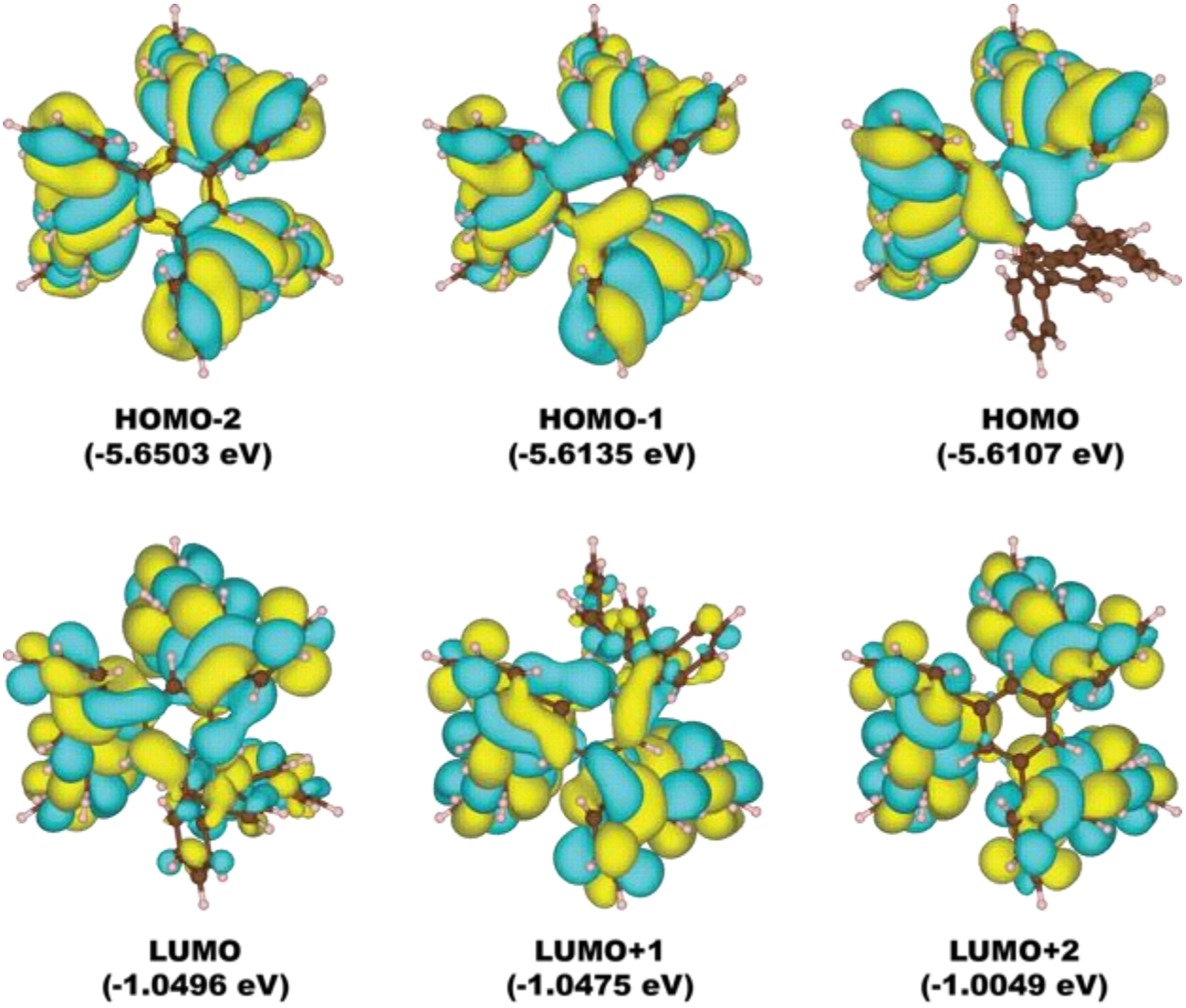


Figure S1. Frontier orbitals of small phenylene cage (**6.6a**).

Table 6.2. Optimized structures of phenylene cages in Cartesian coordinates (Å)

Small Cage (**6.6a**)

C	5.70466	0.15527	-1.40083	C	1.64454	1.19806	4.04962
C	5.70713	-0.15263	1.38377	C	1.35618	1.55510	1.68851
C	5.70562	1.27742	-0.55915	H	3.06066	2.30052	0.62598
C	5.70405	-1.12032	-0.82616	H	3.57595	1.69153	4.84929
C	5.70624	-1.28823	0.56652	H	1.24636	0.91368	5.01985
C	5.70710	1.13738	0.83293	H	0.74267	1.52424	0.79270
H	5.72636	2.27189	-0.99632	C	3.49466	-3.39945	0.42823
H	5.72366	-1.99604	-1.46896	C	0.80458	-3.11933	-0.44964
H	5.72916	-0.27117	2.46355	C	2.95635	-4.25593	-0.54550
C	5.83034	0.32769	-2.88003	C	2.67463	-2.37162	0.92220
C	6.30682	0.76363	-5.61972	C	1.35546	-2.24014	0.49839
C	7.02341	-0.09437	-3.48742	C	1.64158	-4.11399	-0.98225
C	4.84131	0.95449	-3.67266	H	3.57318	-5.05284	-0.95307
C	5.10983	1.17089	-5.03553	H	3.06229	-1.68485	1.66779
C	7.26630	0.11456	-4.84346	H	0.74298	-1.44612	0.91584
H	7.78015	-0.56999	-2.86921	H	1.24225	-4.81527	-1.70991
H	4.34330	1.63727	-5.64832	C	3.49298	1.32923	-3.15920
H	8.20158	-0.21813	-5.28561	C	0.80315	1.95026	-2.47671
H	6.48034	0.93877	-6.67816	C	2.95644	2.60235	-3.40931
C	5.83319	2.33144	1.72306	C	2.67156	0.38629	-2.51977
C	6.31015	4.48201	3.47577	C	1.35248	0.68802	-2.19377
C	7.02675	3.06794	1.66359	C	1.64182	2.91018	-3.06731
C	4.84384	2.70344	2.66239	H	3.57415	3.35478	-3.89308
C	5.11250	3.77341	3.53378	H	3.05760	-0.60407	-2.30045
C	7.26974	4.13582	2.52515	H	0.73899	-0.07186	-1.71826
H	7.78399	2.77164	0.94259	H	1.24415	3.89258	-3.30724
H	4.34565	4.07007	4.24411	C	-0.62809	0.81044	3.05320
H	8.20540	4.68466	2.45981	C	-3.40552	0.31510	3.46200
H	6.48407	5.30935	4.15867	C	-1.60960	1.54240	2.36500
C	5.83220	-2.65594	1.15589	C	-1.06417	-0.21047	3.91436
C	6.31091	-5.24801	2.14383	C	-2.42125	-0.45302	4.11059
C	7.02583	-2.97138	1.82394	C	-2.96543	1.30463	2.56889
C	4.84343	-3.65622	1.00865	H	-1.31027	2.34681	1.69926
C	5.11326	-4.94531	1.50055	H	-2.72729	-1.25120	4.78166
C	7.26986	-4.25087	2.31877	H	-3.68654	1.93085	2.05881
H	7.78238	-2.19807	1.92715	C	-4.84137	0.13965	3.82794
H	4.34708	-5.70954	1.40293	C	-7.49613	-0.18459	4.75044
H	8.20563	-4.46771	2.82698	C	-5.90816	0.03682	2.90239
H	6.48535	-6.25272	2.51962	C	-5.14683	0.07501	5.20145
C	3.49525	2.07163	2.72865	C	-6.44915	-0.08435	5.66496
C	0.80688	1.16602	2.92225	C	-7.21636	-0.12548	3.38741
C	2.67446	1.99083	1.59182	H	-4.33514	0.17631	5.91598
C	2.95862	1.64957	3.95554	H	-6.64305	-0.12123	6.73364

H	-8.02565	-0.21243	2.66738	C	-7.50012	4.20858	-2.20572
H	-8.52062	-0.30721	5.09131	H	-8.02667	2.41553	-1.14380
C	-5.75123	0.02953	1.40978	H	-4.34137	5.04198	-3.10513
C	-5.75785	-0.02987	-1.39103	H	-8.52488	4.56488	-2.26676
C	-5.75829	-1.18969	0.72108	H	-6.65009	5.89811	-3.24863
C	-5.75766	1.21918	0.66934	C	-3.40890	2.84354	-2.00748
C	-5.75103	1.20618	-0.73089	C	-0.63209	2.24175	-2.23616
C	-5.75160	-1.23603	-0.67934	C	-2.96978	1.57823	-2.42786
H	-5.81116	-2.11572	1.28714	C	-2.42419	3.78657	-1.66077
H	-5.80998	2.17234	1.18852	C	-1.06725	3.49550	-1.77501
H	-5.81039	-0.05723	-2.47601	C	-1.61411	1.28277	-2.53395
C	-5.90971	-2.53229	-1.41903	H	-3.69149	0.82626	-2.72148
C	-6.45375	-4.86560	-2.90175	H	-2.72996	4.76448	-1.29849
C	-7.21817	-2.86909	-1.80309	H	-0.33436	4.24921	-1.49895
C	-4.84415	-3.38763	-1.79064	H	-1.31462	0.30662	-2.90455
C	-5.15109	-4.54558	-2.53166	C	-3.40810	-3.16016	-1.45523
C	-7.49945	-4.02068	-2.53406	C	-0.63071	-3.05633	-0.82191
H	-8.02638	-2.19990	-1.52035	C	-2.42413	-3.33867	-2.44471
H	-4.34052	-5.21717	-2.79936	C	-2.96781	-2.88308	-0.15140
H	-8.52408	-4.25302	-2.81150	C	-1.61189	-2.82693	0.15643
H	-6.64889	-5.77349	-3.46630	C	-1.06702	-3.29142	-2.13664
C	-5.90985	2.49597	-1.48183	H	-2.73057	-3.52016	-3.47148
C	-6.45464	4.95265	-2.74967	H	-3.68904	-2.75411	0.64585
C	-7.21849	2.99694	-1.57938	H	-1.31173	-2.65389	1.18594
C	-4.84475	3.24825	-2.03391	H	-0.33498	-3.43463	-2.92718
C	-5.15191	4.47188	-2.66035	H	-0.33182	-0.82344	4.43326

Medium Cage (**6.6c**)

H	4.02298	6.53988	-2.37008	H	2.37038	11.01794	-2.24979
C	4.21624	6.35075	-1.31796	H	-0.09472	10.76151	-1.90702
C	4.76520	5.93041	1.39359	C	0.29314	6.54473	-0.04643
C	3.38680	6.93729	-0.35340	C	-1.13979	4.24124	0.81995
C	5.31945	5.56432	-0.95441	C	-0.83098	6.65227	0.79320
C	5.58089	5.35941	0.40468	C	0.69452	5.25443	-0.42989
C	3.67099	6.71526	1.00253	C	-0.00441	4.13025	-0.00065
H	6.44629	4.77335	0.70121	C	-1.53907	5.52766	1.21115
H	3.05205	7.18405	1.76269	H	-1.14901	7.63389	1.13377
C	2.34019	7.92113	-0.78235	H	1.53794	5.12559	-1.09946
C	0.59227	9.97996	-1.59350	H	0.30251	3.15038	-0.35479
C	2.81753	9.09637	-1.38777	H	-2.39536	5.64629	1.87024
C	0.94367	7.76889	-0.59384	C	-1.86409	3.01771	1.24724
C	0.09982	8.81661	-1.01074	C	-3.16153	0.57654	1.93091
C	1.96469	10.12079	-1.79000	C	-3.25695	2.87892	1.13050
H	3.89017	9.20698	-1.52103	C	-1.14218	1.92798	1.75673
H	-0.97352	8.68990	-0.90590	C	-1.77529	0.74053	2.09696

C	-3.89238	1.68069	1.46027	C	3.76290	3.41981	-4.10360
H	-3.84284	3.70212	0.72986	C	4.33897	2.57057	-1.93142
H	-0.07348	2.03285	1.91569	C	3.21958	1.74692	-1.95701
H	-1.19479	-0.06822	2.52888	C	2.62458	2.61665	-4.11527
H	-4.96498	1.58887	1.30980	H	3.96406	4.07548	-4.94719
C	5.15032	5.82363	2.83556	H	5.00798	2.53168	-1.07722
C	6.09291	5.81742	5.49096	H	3.05991	1.06416	-1.12868
C	5.49127	7.01637	3.49376	H	1.94564	2.68160	-4.96045
C	5.25939	4.59823	3.53912	C	1.14218	0.86203	-3.06310
C	5.74061	4.62717	4.86086	C	-1.14218	-0.86203	-3.06310
C	5.95695	7.02420	4.80652	C	0.55756	0.41620	-4.26169
H	5.41359	7.95052	2.94402	C	0.55267	0.42005	-1.86644
H	5.79637	3.69413	5.41413	C	-0.55267	-0.42005	-1.86644
H	6.21845	7.96415	5.28504	C	-0.55756	-0.41620	-4.26169
H	6.45290	5.80165	6.51623	H	0.98927	0.71041	-5.21384
C	4.80471	3.28806	2.99496	H	0.95840	0.73760	-0.91144
C	3.77885	0.73563	2.24598	H	-0.95840	-0.73760	-0.91144
C	5.53608	2.10871	3.22273	H	-0.98927	-0.71041	-5.21384
C	3.56974	3.16695	2.33813	H	-6.44629	-4.77335	0.70121
C	3.07552	1.92188	1.97132	C	-5.58089	-5.35941	0.40468
C	5.03678	0.85936	2.85686	C	-3.38680	-6.93729	-0.35340
H	6.50704	2.16998	3.70708	C	-4.76520	-5.93041	1.39359
H	2.97611	4.05072	2.13182	C	-5.31945	-5.56432	-0.95441
H	2.12060	1.86990	1.45802	C	-4.21624	-6.35075	-1.31796
H	5.61350	-0.03281	3.08656	C	-3.67099	-6.71526	1.00253
C	3.16153	-0.57654	1.93091	H	-4.02298	-6.53988	-2.37008
C	1.77529	-0.74053	2.09696	H	-3.05205	-7.18405	1.76269
C	3.89238	-1.68069	1.46027	C	-5.15032	-5.82363	2.83556
C	3.25695	-2.87892	1.13050	C	-6.09291	-5.81742	5.49096
C	1.14218	-1.92798	1.75673	C	-5.49127	-7.01637	3.49376
H	1.19479	0.06822	2.52888	C	-5.25939	-4.59823	3.53912
H	4.96498	-1.58887	1.30980	C	-5.74061	-4.62717	4.86086
H	3.84284	-3.70212	0.72986	C	-5.95695	-7.02420	4.80652
H	0.07348	-2.03285	1.91569	H	-5.41359	-7.95052	2.94402
C	6.27399	5.09942	-2.00847	H	-5.79637	-3.69413	5.41413
C	8.09445	4.52874	-4.07923	H	-6.21845	-7.96415	5.28504
C	7.55259	5.67857	-2.03285	H	-6.45290	-5.80165	6.51623
C	5.91733	4.18627	-3.02735	C	-4.80471	-3.28806	2.99496
C	6.83659	3.93022	-4.05816	C	-3.77885	-0.73563	2.24598
C	8.46119	5.39668	-3.05115	C	-3.56974	-3.16695	2.33813
H	7.81884	6.38490	-1.25094	C	-5.53608	-2.10871	3.22273
H	6.56234	3.22008	-4.83367	C	-5.03678	-0.85936	2.85686
H	9.44257	5.86355	-3.04766	C	-3.07552	-1.92188	1.97132
H	8.78824	4.30528	-4.88536	H	-2.97611	-4.05072	2.13182
C	4.64276	3.41424	-3.01085	H	-6.50704	-2.16998	3.70708
C	2.33195	1.74824	-3.04869	H	-5.61350	0.03281	3.08656

H	-2.12060	-1.86990	1.45802	C	-6.27399	-5.09942	-2.00847
C	-2.34019	-7.92113	-0.78235	C	-8.09445	-4.52874	-4.07923
C	-0.59227	-9.97996	-1.59350	C	-7.55259	-5.67857	-2.03285
C	-2.81753	-9.09637	-1.38777	C	-5.91733	-4.18627	-3.02735
C	-0.94367	-7.76889	-0.59384	C	-6.83659	-3.93022	-4.05816
C	-0.09982	-8.81661	-1.01074	C	-8.46119	-5.39668	-3.05115
C	-1.96469	-10.12079	-1.79000	H	-7.81884	-6.38490	-1.25094
H	-3.89017	-9.20698	-1.52103	H	-6.56234	-3.22008	-4.83367
H	0.97352	-8.68990	-0.90590	H	-9.44257	-5.86355	-3.04766
H	-2.37038	-11.01794	-2.24979	H	-8.78824	-4.30528	-4.88536
H	0.09472	-10.76151	-1.90702	C	-4.64276	-3.41424	-3.01085
C	-0.29314	-6.54473	-0.04643	C	-2.33195	-1.74824	-3.04869
C	1.13979	-4.24124	0.81995	C	-4.33897	-2.57057	-1.93142
C	0.83098	-6.65227	0.79320	C	-3.76290	-3.41981	-4.10360
C	-0.69452	-5.25443	-0.42989	C	-2.62458	-2.61665	-4.11527
C	0.00441	-4.13025	-0.00065	C	-3.21958	-1.74692	-1.95701
C	1.53907	-5.52766	1.21115	H	-5.00798	-2.53168	-1.07722
H	1.14901	-7.63389	1.13377	H	-3.96406	-4.07548	-4.94719
H	-1.53794	-5.12559	-1.09946	H	-1.94564	-2.68160	-4.96045
H	-0.30251	-3.15038	-0.35479	H	-3.05991	-1.06416	-1.12868
H	2.39536	-5.64629	1.87024	C	1.86409	-3.01771	1.24724

Large Cage (**6.6b**)

H	9.92778	-0.07526	2.58314	C	6.99739	-2.42393	1.22008
C	9.91771	-0.00321	1.49897	C	5.66048	-2.38173	0.83737
C	9.97423	0.18987	-1.29650	C	6.01809	-4.24853	-0.63881
C	9.97494	-1.17162	0.73025	H	8.00536	-5.06537	-0.65662
C	9.89450	1.26272	0.89425	H	7.36509	-1.70678	1.94712
C	9.91963	1.34519	-0.50300	H	5.01010	-1.62351	1.26481
C	10.00059	-1.06021	-0.66770	H	5.64266	-4.97648	-1.35332
H	9.93062	2.32109	-0.98062	C	3.69218	-3.29777	-0.42025
H	10.07446	-1.95995	-1.27237	C	0.90589	-3.24731	-1.00748
C	10.16897	-2.50956	1.37072	C	2.73601	-3.15562	0.59890
C	10.80529	-5.04162	2.42670	C	3.22518	-3.43796	-1.73816
C	11.38523	-2.73812	2.03393	C	1.86168	-3.40566	-2.02629
C	9.23766	-3.56850	1.26585	C	1.37567	-3.13971	0.31245
C	9.58573	-4.82581	1.78973	H	3.06500	-3.06488	1.62990
C	11.70650	-3.98643	2.56305	H	3.94004	-3.55357	-2.54886
H	12.09824	-1.92115	2.10532	H	1.53262	-3.51807	-3.05591
H	8.86297	-5.63439	1.72299	H	0.66626	-3.01833	1.12591
H	12.65793	-4.13441	3.06682	C	10.15191	0.29690	-2.77853
H	11.04095	-6.02365	2.82807	C	10.73440	0.59003	-5.51773
C	7.86399	-3.40435	0.71055	C	11.40066	-0.07343	-3.30260
C	5.13854	-3.30386	-0.08659	C	9.16248	0.80156	-3.65504
C	7.35198	-4.30379	-0.23866	C	9.48476	0.94489	-5.01686

C	11.69787	0.06651	-4.65654	C	0.61828	0.79599	2.93860
H	12.15582	-0.45469	-2.62046	C	2.66191	1.62452	3.97920
H	8.71941	1.30953	-5.69615	C	2.74330	0.75880	1.74340
H	12.67540	-0.22432	-5.03165	C	1.37759	0.50353	1.79297
H	10.94650	0.70700	-6.57716	C	1.29726	1.36001	4.03256
C	7.77138	1.12199	-3.23069	H	3.13955	2.08945	4.83664
C	5.02044	1.61073	-2.67881	H	3.28414	0.51042	0.83562
C	7.13424	2.29036	-3.68104	H	0.89404	0.09021	0.91380
C	7.01291	0.22061	-2.46589	H	0.75215	1.58418	4.94522
C	5.66939	0.45979	-2.19799	H	-10.07365	-2.39311	0.42275
C	5.79009	2.53126	-3.40998	C	-9.99728	-1.31778	0.28439
H	7.69876	3.01441	-4.26278	C	-9.95600	1.45664	-0.08175
H	7.47014	-0.69042	-2.09498	C	-9.87705	-0.79788	-1.01262
H	5.11718	-0.26444	-1.60631	C	-10.08181	-0.47877	1.40242
H	5.32085	3.42722	-3.80689	C	-10.08380	0.90674	1.20166
C	3.56804	1.81836	-2.46290	C	-9.83156	0.59181	-1.17973
C	0.75754	2.19164	-2.14145	H	-10.21545	1.57108	2.05157
C	2.68150	0.72694	-2.46015	H	-9.77082	1.00749	-2.18130
C	3.01662	3.09942	-2.28647	C	-10.05995	-1.70148	-2.20002
C	1.64568	3.28125	-2.12836	C	-10.74772	-3.33419	-4.39430
C	1.31246	0.91050	-2.30441	C	-11.38524	-1.80238	-2.65913
H	3.06258	-0.27708	-2.62183	C	-9.04754	-2.42907	-2.87088
H	3.67353	3.96399	-2.24400	C	-9.43077	-3.24222	-3.95800
H	1.26157	4.28350	-1.96086	C	-11.73791	-2.60175	-3.74256
H	0.65748	0.04610	-2.34574	H	-12.15115	-1.23062	-2.14241
C	10.01258	2.49377	1.73759	H	-8.66785	-3.83442	-4.45391
C	10.50660	4.69849	3.41872	H	-12.77385	-2.65548	-4.06616
C	11.23770	3.17912	1.70098	H	-10.99663	-3.97986	-5.23227
C	9.00095	2.94659	2.61549	C	-7.59457	-2.40574	-2.53502
C	9.27916	4.04181	3.45278	C	-4.79162	-2.63725	-2.03356
C	11.48972	4.27304	2.52618	C	-6.65340	-2.37987	-3.58112
H	12.01141	2.82149	1.02686	C	-7.09357	-2.50603	-1.22713
H	8.49600	4.39957	4.11548	C	-5.72633	-2.61442	-0.98435
H	12.44956	4.78031	2.47822	C	-5.29058	-2.49956	-3.33980
H	10.68589	5.54697	4.07371	H	-6.99954	-2.27133	-4.60482
C	7.62175	2.38334	2.65054	H	-7.77406	-2.51708	-0.38435
C	4.87313	1.63887	2.76868	H	-5.38615	-2.67388	0.04556
C	7.01108	2.04596	3.86916	H	-4.60728	-2.51766	-4.18370
C	6.84189	2.29859	1.48614	C	-3.34017	-2.81439	-1.78421
C	5.49750	1.94540	1.54579	C	-0.54535	-3.14722	-1.29921
C	5.67157	1.67083	3.92575	C	-2.86950	-3.55759	-0.68608
H	7.59733	2.07440	4.78418	C	-2.37605	-2.26293	-2.64608
H	7.27827	2.55781	0.52674	C	-1.01459	-2.43525	-2.41610
H	4.91518	1.95863	0.62980	C	-1.50748	-3.71313	-0.44444
H	5.24282	1.39216	4.88408	H	-3.58103	-4.04851	-0.02824
C	3.42290	1.32940	2.83375	H	-2.69250	-1.65510	-3.48807

H	-0.30231	-1.97290	-3.09389	H	-0.78362	4.27908	-3.00978
H	-1.18367	-4.31077	0.40339	C	-10.31255	-1.07810	2.75732
C	-10.13978	2.92843	-0.28234	C	-10.90621	-2.35107	5.19873
C	-10.76522	5.63949	-0.72745	C	-11.62654	-1.44670	3.08681
C	-11.40064	3.45341	0.04771	C	-9.27563	-1.34941	3.67830
C	-9.15995	3.79271	-0.82651	C	-9.59704	-1.99325	4.88583
C	-9.50510	5.13992	-1.04317	C	-11.93018	-2.07162	4.29467
C	-11.71994	4.79181	-0.16759	H	-12.41770	-1.24227	2.37035
H	-12.14939	2.78045	0.45682	H	-8.79758	-2.19893	5.59255
H	-8.74690	5.81217	-1.43428	H	-12.95752	-2.34234	4.52313
H	-12.70677	5.16451	0.09338	H	-11.12349	-2.84069	6.14427
H	-10.99206	6.68777	-0.90267	C	-7.84284	-1.00219	3.43906
C	-7.75698	3.38578	-1.11439	C	-5.07558	-0.37612	3.19716
C	-4.98343	2.89847	-1.54242	C	-6.87047	-2.01331	3.39742
C	-7.11018	3.82848	-2.28077	C	-7.40548	0.32797	3.34982
C	-6.99547	2.65627	-0.18705	C	-6.05143	0.63452	3.23439
C	-5.64072	2.42172	-0.39514	C	-5.51685	-1.70807	3.27363
C	-5.75613	3.58792	-2.49208	H	-7.18153	-3.05185	3.47609
H	-7.68053	4.36263	-3.03615	H	-8.13170	1.13344	3.39636
H	-7.45725	2.29978	0.72752	H	-5.74678	1.67537	3.16589
H	-5.07486	1.89709	0.36897	H	-4.78714	-2.51314	3.27797
H	-5.29461	3.92803	-3.41498	C	-3.62956	-0.05584	3.10790
C	-3.52480	2.70563	-1.72098	C	-0.83710	0.51610	2.98977
C	-0.70649	2.37330	-1.99662	C	-3.08054	1.04583	3.78625
C	-2.73312	3.67774	-2.35709	C	-2.75199	-0.85622	2.35739
C	-2.87445	1.56021	-1.23226	C	-1.39097	-0.57697	2.30113
C	-1.49997	1.40097	-1.36354	C	-1.71852	1.32525	3.72772
C	-1.35844	3.51433	-2.49477	H	-3.72649	1.68101	4.38619
H	-3.19757	4.58621	-2.73030	H	-3.13859	-1.70207	1.79617
H	-3.45116	0.77628	-0.75092	H	-0.74529	-1.22907	1.72136
H	-1.03691	0.51030	-0.95130	H	-1.33509	2.19555	4.25258

Single Crystal Diffraction Data

X-ray Experimental for **6.6a** $C_{84}H_{54} – 0.64\ C_5H_{12} – 0.36\ CHCl_3$: Crystals grew as colorless needles by vapor diffusion of *n*-pentane into a chloroform solution. The crystal collected for diffraction experiments had approximate dimensions; 0.24 x 0.15 x 0.12 mm. The data was collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 1104 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data was collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S3. Data reduction was performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[32] The structure was solved by direct methods using SIR2004[33] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[34] Structure analysis was aided by use of the programs PLATON98[35] and WinGX.[36] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

A mixture of the crystallization solvents, chloroform and n-pentane, were disordered in a space between adjacent molecules of the polyaromatic molecule. The geometry of the two molecules was restrained throughout the refinement procedure. The variable x was assigned to the site occupancy factors for the elements of the chloroform molecule. The variable (1-x) was assigned to the site occupancy factors for the atoms of n-pentane. A common isotropic displacement parameter was refined while refining the variable x. In this way, the site occupancy for the atoms of the chloroform molecule refined to 36(2)%.

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0597*P)^2 + (6.7897*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.181, with R(F) equal to 0.0798 and a goodness of fit, S, = 1.07. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[37] The data were checked for secondary extinction effects, but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[38] All figures were generated using SHELXTL/PC.[39] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 6.3. Crystal data and structure refinement for **6.6a**.

Empirical formula	$C_{87.56}H_{62.04}Cl_{1.08}$	
Formula weight	1152.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 17.3858(10) Å	α= 90°.
	b = 18.7514(9) Å	β= 110.071(2)°.
	c = 20.2251(12) Å	γ = 90°.
Volume	6193.1(6) $Å^3$	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	0.115 mm^{-1}	
F(000)	2423	
Crystal size	0.240 x 0.150 x 0.120 mm^3	
Theta range for data collection	3.007 to 27.454°.	
Index ranges	-22<=h<=22, -24<=k<=23, -26<=l<=26	
Reflections collected	99296	
Independent reflections	14126 [R(int) = 0.0836]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.740	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14126 / 675 / 842	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0798, wR2 = 0.1612	
R indices (all data)	R1 = 0.1251, wR2 = 0.1811	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.864 and -0.436 $e.Å^{-3}$	

Table 6.4. Atomic coordinates (Å x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **6.6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	7330(2)	1360(1)	4061(1)	22(1)
C2	7445(1)	1521(1)	4762(1)	22(1)
C3	7575(1)	2221(1)	5007(1)	21(1)
C4	7600(2)	2764(1)	4542(1)	22(1)
C5	7489(2)	2621(1)	3839(1)	23(1)
C6	7344(2)	1914(1)	3604(1)	23(1)
C7	7304(2)	600(1)	3819(1)	23(1)
C8	7975(2)	375(2)	3647(1)	28(1)
C9	8056(2)	-323(2)	3454(2)	31(1)
C10	7448(2)	-811(2)	3424(2)	32(1)
C11	6770(2)	-598(2)	3577(2)	31(1)
C12	6675(2)	104(1)	3780(1)	25(1)
C13	5893(2)	282(1)	3895(1)	25(1)
C14	5471(2)	-232(1)	4139(2)	28(1)
C15	4704(2)	-99(1)	4185(1)	27(1)
C16	4318(2)	562(1)	3995(1)	24(1)
C17	4746(2)	1078(1)	3755(1)	25(1)
C18	5507(2)	945(1)	3704(1)	26(1)
C19	3507(2)	725(1)	4055(1)	24(1)
C20	2975(2)	199(1)	4134(1)	25(1)
C21	2228(2)	366(1)	4199(1)	26(1)
C22	1967(2)	1071(1)	4184(1)	22(1)
C23	2493(2)	1600(1)	4110(1)	26(1)
C24	3239(2)	1430(1)	4048(2)	28(1)
C25	1183(2)	1261(1)	4291(1)	24(1)
C26	980(2)	919(2)	4826(2)	32(1)
C27	287(2)	1107(2)	4981(2)	37(1)
C28	-217(2)	1646(2)	4607(2)	35(1)
C29	-30(2)	1987(2)	4066(1)	28(1)
C30	655(2)	1790(1)	3893(1)	23(1)
C31	7753(2)	2396(1)	5767(1)	21(1)
C32	8478(2)	2136(1)	6257(1)	24(1)
C33	8715(2)	2320(1)	6964(1)	25(1)
C34	8226(2)	2771(2)	7191(1)	26(1)
C35	7504(2)	3030(1)	6708(1)	24(1)
C36	7247(2)	2842(1)	6002(1)	22(1)
C37	6420(2)	3082(1)	5531(1)	24(1)
C38	5862(2)	2603(1)	5088(1)	25(1)
C39	5066(2)	2803(1)	4726(1)	26(1)
C40	4778(2)	3486(2)	4778(2)	30(1)
C41	5333(2)	3964(2)	5217(2)	44(1)

C42	6135(2)	3766(2)	5582(2)	40(1)
C43	3908(2)	3693(2)	4382(2)	32(1)
C44	3482(2)	3383(2)	3740(2)	31(1)
C45	2697(2)	3597(2)	3334(2)	30(1)
C46	2310(2)	4148(1)	3560(2)	28(1)
C47	2704(2)	4425(2)	4228(2)	40(1)
C48	3493(2)	4207(2)	4634(2)	42(1)
C49	1524(2)	4456(1)	3080(1)	25(1)
C50	878(2)	4038(1)	2636(1)	23(1)
C51	209(2)	4373(1)	2148(1)	27(1)
C52	167(2)	5105(2)	2075(2)	30(1)
C53	800(2)	5519(2)	2512(2)	29(1)
C54	1464(2)	5194(1)	3013(2)	28(1)
C55	7601(2)	3203(1)	3372(1)	24(1)
C56	8362(2)	3545(2)	3592(1)	29(1)
C57	8544(2)	4075(2)	3184(2)	37(1)
C58	7960(2)	4274(2)	2554(2)	38(1)
C59	7198(2)	3946(2)	2338(2)	33(1)
C60	7003(2)	3413(2)	2734(1)	27(1)
C61	6152(2)	3116(1)	2481(1)	25(1)
C62	5699(2)	3048(2)	2931(2)	31(1)
C63	4892(2)	2829(2)	2676(2)	33(1)
C64	4494(2)	2661(2)	1969(1)	27(1)
C65	4954(2)	2720(2)	1523(2)	29(1)
C66	5758(2)	2947(2)	1774(1)	28(1)
C67	3622(2)	2428(2)	1710(1)	28(1)
C68	3288(2)	2084(2)	2166(2)	32(1)
C69	2481(2)	1860(2)	1948(1)	30(1)
C70	1965(2)	1975(1)	1255(1)	24(1)
C71	2287(2)	2325(2)	801(1)	28(1)
C72	3097(2)	2548(2)	1020(1)	29(1)
C73	1123(2)	1668(1)	997(1)	24(1)
C74	583(2)	1693(1)	1383(1)	23(1)
C75	-170(2)	1341(2)	1115(2)	29(1)
C76	-394(2)	965(2)	488(2)	34(1)
C77	134(2)	944(2)	106(2)	33(1)
C78	878(2)	1288(2)	361(1)	30(1)
C79	766(1)	2148(1)	3268(1)	21(1)
C80	836(1)	2889(1)	3258(1)	22(1)
C81	868(1)	3244(1)	2660(1)	22(1)
C82	819(1)	2848(1)	2061(1)	23(1)
C83	742(1)	2109(1)	2054(1)	22(1)
C84	736(1)	1766(1)	2664(1)	22(1)
Cl1	4595(2)	4617(1)	3347(2)	68(1)
Cl2	6206(3)	5016(3)	3342(3)	122(2)
Cl3	4932(3)	6048(2)	3070(2)	90(1)

C1A	5159(5)	5158(4)	2982(8)	85(3)
C1B	4131(6)	5481(6)	2989(5)	126(3)
C2B	4847(4)	4994(5)	3193(5)	99(2)
C3B	5654(4)	5357(5)	3412(5)	103(2)
C4B	6342(5)	4814(6)	3723(5)	99(3)
C5B	7151(4)	5117(4)	3899(4)	77(2)

Table 6.5. Bond lengths [Å] and angles [°] for **6.6a**.

C1-C6	1.396(4)	C24-H24	0.95
C1-C2	1.396(4)	C25-C30	1.403(4)
C1-C7	1.503(4)	C25-C26	1.403(4)
C2-C3	1.393(4)	C26-C27	1.392(4)
C2-H2	0.95	C26-H26	0.95
C3-C4	1.397(4)	C27-C28	1.381(4)
C3-C31	1.497(4)	C27-H27	0.95
C4-C5	1.394(4)	C28-C29	1.397(4)
C4-H4	0.95	C28-H28	0.95
C5-C6	1.401(4)	C29-C30	1.402(4)
C5-C55	1.500(4)	C29-H29	0.95
C6-H6	0.95	C30-C79	1.502(4)
C7-C8	1.392(4)	C31-C32	1.397(3)
C7-C12	1.416(4)	C31-C36	1.409(4)
C8-C9	1.387(4)	C32-C33	1.388(4)
C8-H8	0.95	C32-H32	0.95
C9-C10	1.383(4)	C33-C34	1.384(4)
C9-H9	0.95	C33-H33	0.95
C10-C11	1.377(4)	C34-C35	1.388(4)
C10-H10	0.95	C34-H34	0.95
C11-C12	1.406(4)	C35-C36	1.389(4)
C11-H11	0.95	C35-H35	0.95
C12-C13	1.494(4)	C36-C37	1.496(3)
C13-C14	1.400(4)	C37-C42	1.391(4)
C13-C18	1.402(4)	C37-C38	1.397(4)
C14-C15	1.392(4)	C38-C39	1.377(3)
C14-H14	0.95	C38-H38	0.95
C15-C16	1.399(4)	C39-C40	1.391(4)
C15-H15	0.95	C39-H39	0.95
C16-C17	1.405(4)	C40-C41	1.390(4)
C16-C19	1.487(4)	C40-C43	1.500(4)
C17-C18	1.384(4)	C41-C42	1.387(4)
C17-H17	0.95	C41-H41	0.95
C18-H18	0.95	C42-H42	0.95
C19-C20	1.399(4)	C43-C44	1.384(4)
C19-C24	1.401(4)	C43-C48	1.401(4)
C20-C21	1.386(4)	C44-C45	1.389(4)
C20-H20	0.95	C44-H44	0.95
C21-C22	1.394(4)	C45-C46	1.394(4)
C21-H21	0.95	C45-H45	0.95
C22-C23	1.391(4)	C46-C47	1.390(4)
C22-C25	1.494(4)	C46-C49	1.493(3)
C23-C24	1.382(4)	C47-C48	1.397(4)
C23-H23	0.95	C47-H47	0.95

C48-H48	0.95	C71-H71	0.95
C49-C54	1.390(4)	C72-H72	0.95
C49-C50	1.412(4)	C73-C78	1.402(4)
C50-C51	1.391(3)	C73-C74	1.413(4)
C50-C81	1.489(4)	C74-C75	1.399(4)
C51-C52	1.379(4)	C74-C83	1.505(4)
C51-H51	0.95	C75-C76	1.385(4)
C52-C53	1.389(4)	C75-H75	0.95
C52-H52	0.95	C76-C77	1.390(4)
C53-C54	1.389(4)	C76-H76	0.95
C53-H53	0.95	C77-C78	1.377(4)
C54-H54	0.95	C77-H77	0.95
C55-C56	1.398(4)	C78-H78	0.95
C55-C60	1.407(4)	C79-C80	1.395(4)
C56-C57	1.394(4)	C79-C84	1.401(4)
C56-H56	0.95	C80-C81	1.398(4)
C57-C58	1.380(4)	C80-H80	0.95
C57-H57	0.95	C81-C82	1.399(4)
C58-C59	1.388(4)	C82-C83	1.393(4)
C58-H58	0.95	C82-H82	0.95
C59-C60	1.393(4)	C83-C84	1.395(4)
C59-H59	0.95	C84-H84	0.95
C60-C61	1.497(4)	Cl1-C1A	1.744(7)
C61-C66	1.394(4)	Cl2-C1A	1.733(8)
C61-C62	1.399(4)	Cl3-C1A	1.737(8)
C62-C63	1.382(4)	C1A-H1AA	1.00
C62-H62	0.95	C1B-C2B	1.483(8)
C63-C64	1.395(4)	C1B-H1B1	0.98
C63-H63	0.95	C1B-H1B2	0.98
C64-C65	1.399(4)	C1B-H1B3	0.98
C64-C67	1.489(4)	C2B-C3B	1.483(8)
C65-C66	1.382(4)	C2B-H2B1	0.99
C65-H65	0.95	C2B-H2B2	0.99
C66-H66	0.95	C3B-C4B	1.532(8)
C67-C72	1.399(4)	C3B-H3B1	0.99
C67-C68	1.404(4)	C3B-H3B2	0.99
C68-C69	1.382(4)	C4B-C5B	1.444(8)
C68-H68	0.95	C4B-H4B1	0.99
C69-C70	1.398(4)	C4B-H4B2	0.99
C69-H69	0.95	C5B-H5B1	0.98
C70-C71	1.393(4)	C5B-H5B2	0.98
C70-C73	1.492(4)	C5B-H5B3	0.98
C71-C72	1.388(4)		

C6-C1-C2	118.9(2)	C2-C1-C7	120.9(2)
C6-C1-C7	119.8(2)	C3-C2-C1	120.9(2)

C3-C2-H2	119.6	C16-C17-H17	118.9
C1-C2-H2	119.6	C17-C18-C13	121.3(3)
C2-C3-C4	119.1(2)	C17-C18-H18	119.3
C2-C3-C31	121.5(2)	C13-C18-H18	119.3
C4-C3-C31	119.2(2)	C20-C19-C24	115.7(2)
C5-C4-C3	121.4(2)	C20-C19-C16	123.2(2)
C5-C4-H4	119.3	C24-C19-C16	121.0(2)
C3-C4-H4	119.3	C21-C20-C19	122.0(2)
C4-C5-C6	118.3(2)	C21-C20-H20	119.0
C4-C5-C55	119.9(2)	C19-C20-H20	119.0
C6-C5-C55	121.6(2)	C20-C21-C22	121.4(2)
C1-C6-C5	121.5(2)	C20-C21-H21	119.3
C1-C6-H6	119.3	C22-C21-H21	119.3
C5-C6-H6	119.3	C23-C22-C21	117.2(2)
C8-C7-C12	118.9(2)	C23-C22-C25	120.8(2)
C8-C7-C1	115.7(2)	C21-C22-C25	121.9(2)
C12-C7-C1	125.3(2)	C24-C23-C22	121.1(3)
C9-C8-C7	122.1(3)	C24-C23-H23	119.4
C9-C8-H8	118.9	C22-C23-H23	119.4
C7-C8-H8	118.9	C23-C24-C19	122.5(2)
C10-C9-C8	119.1(3)	C23-C24-H24	118.7
C10-C9-H9	120.4	C19-C24-H24	118.7
C8-C9-H9	120.4	C30-C25-C26	118.6(2)
C11-C10-C9	119.9(3)	C30-C25-C22	122.4(2)
C11-C10-H10	120.0	C26-C25-C22	119.0(2)
C9-C10-H10	120.0	C27-C26-C25	121.6(3)
C10-C11-C12	122.2(3)	C27-C26-H26	119.2
C10-C11-H11	118.9	C25-C26-H26	119.2
C12-C11-H11	118.9	C28-C27-C26	119.8(3)
C11-C12-C7	117.7(2)	C28-C27-H27	120.1
C11-C12-C13	117.4(2)	C26-C27-H27	120.1
C7-C12-C13	124.7(2)	C27-C28-C29	119.4(3)
C14-C13-C18	116.6(2)	C27-C28-H28	120.3
C14-C13-C12	121.0(2)	C29-C28-H28	120.3
C18-C13-C12	122.1(2)	C28-C29-C30	121.3(3)
C15-C14-C13	122.1(3)	C28-C29-H29	119.3
C15-C14-H14	119.0	C30-C29-H29	119.3
C13-C14-H14	119.0	C29-C30-C25	119.2(2)
C14-C15-C16	121.3(3)	C29-C30-C79	117.3(2)
C14-C15-H15	119.3	C25-C30-C79	123.5(2)
C16-C15-H15	119.3	C32-C31-C36	118.9(2)
C15-C16-C17	116.4(2)	C32-C31-C3	118.0(2)
C15-C16-C19	122.5(2)	C36-C31-C3	123.0(2)
C17-C16-C19	121.1(2)	C33-C32-C31	121.4(2)
C18-C17-C16	122.3(2)	C33-C32-H32	119.3
C18-C17-H17	118.9	C31-C32-H32	119.3

C34-C33-C32	119.6(2)	C47-C48-H48	119.6
C34-C33-H33	120.2	C43-C48-H48	119.6
C32-C33-H33	120.2	C54-C49-C50	118.3(2)
C33-C34-C35	119.4(2)	C54-C49-C46	118.0(2)
C33-C34-H34	120.3	C50-C49-C46	123.3(2)
C35-C34-H34	120.3	C51-C50-C49	119.3(2)
C34-C35-C36	121.9(2)	C51-C50-C81	117.3(2)
C34-C35-H35	119.1	C49-C50-C81	123.4(2)
C36-C35-H35	119.1	C52-C51-C50	121.7(2)
C35-C36-C31	118.7(2)	C52-C51-H51	119.1
C35-C36-C37	118.5(2)	C50-C51-H51	119.1
C31-C36-C37	122.6(2)	C51-C52-C53	119.2(2)
C42-C37-C38	117.0(2)	C51-C52-H52	120.4
C42-C37-C36	121.3(2)	C53-C52-H52	120.4
C38-C37-C36	121.2(2)	C54-C53-C52	119.8(3)
C39-C38-C37	121.0(2)	C54-C53-H53	120.1
C39-C38-H38	119.5	C52-C53-H53	120.1
C37-C38-H38	119.5	C53-C54-C49	121.6(2)
C38-C39-C40	122.1(2)	C53-C54-H54	119.2
C38-C39-H39	118.9	C49-C54-H54	119.2
C40-C39-H39	118.9	C56-C55-C60	118.9(2)
C41-C40-C39	117.0(2)	C56-C55-C5	116.6(2)
C41-C40-C43	121.6(3)	C60-C55-C5	124.4(2)
C39-C40-C43	121.4(2)	C57-C56-C55	121.4(3)
C42-C41-C40	121.2(3)	C57-C56-H56	119.3
C42-C41-H41	119.4	C55-C56-H56	119.3
C40-C41-H41	119.4	C58-C57-C56	119.6(3)
C41-C42-C37	121.7(3)	C58-C57-H57	120.2
C41-C42-H42	119.1	C56-C57-H57	120.2
C37-C42-H42	119.1	C57-C58-C59	119.4(3)
C44-C43-C48	117.0(3)	C57-C58-H58	120.3
C44-C43-C40	120.6(3)	C59-C58-H58	120.3
C48-C43-C40	122.4(3)	C58-C59-C60	122.1(3)
C43-C44-C45	122.3(3)	C58-C59-H59	119.0
C43-C44-H44	118.9	C60-C59-H59	119.0
C45-C44-H44	118.9	C59-C60-C55	118.6(2)
C44-C45-C46	120.5(3)	C59-C60-C61	118.5(2)
C44-C45-H45	119.7	C55-C60-C61	122.9(2)
C46-C45-H45	119.7	C66-C61-C62	117.3(2)
C47-C46-C45	117.7(2)	C66-C61-C60	121.0(2)
C47-C46-C49	121.5(2)	C62-C61-C60	121.5(2)
C45-C46-C49	120.7(2)	C63-C62-C61	120.7(3)
C46-C47-C48	121.3(3)	C63-C62-H62	119.6
C46-C47-H47	119.4	C61-C62-H62	119.6
C48-C47-H47	119.4	C62-C63-C64	122.2(3)
C47-C48-C43	120.8(3)	C62-C63-H63	118.9

C64-C63-H63	118.9	C80-C79-C84	118.3(2)
C63-C64-C65	116.9(2)	C80-C79-C30	119.7(2)
C63-C64-C67	120.8(2)	C84-C79-C30	121.8(2)
C65-C64-C67	122.3(2)	C79-C80-C81	121.1(2)
C66-C65-C64	121.2(3)	C79-C80-H80	119.5
C66-C65-H65	119.4	C81-C80-H80	119.5
C64-C65-H65	119.4	C80-C81-C82	119.2(2)
C65-C66-C61	121.7(3)	C80-C81-C50	120.5(2)
C65-C66-H66	119.1	C82-C81-C50	120.0(2)
C61-C66-H66	119.1	C83-C82-C81	120.9(2)
C72-C67-C68	116.9(2)	C83-C82-H82	119.5
C72-C67-C64	122.7(2)	C81-C82-H82	119.5
C68-C67-C64	120.4(2)	C82-C83-C84	118.6(2)
C69-C68-C67	122.3(3)	C82-C83-C74	120.8(2)
C69-C68-H68	118.9	C84-C83-C74	120.3(2)
C67-C68-H68	118.9	C83-C84-C79	121.8(2)
C68-C69-C70	120.3(3)	C83-C84-H84	119.1
C68-C69-H69	119.9	C79-C84-H84	119.1
C70-C69-H69	119.9	Cl2-C1A-Cl3	110.3(6)
C71-C70-C69	118.0(2)	Cl2-C1A-Cl1	113.2(6)
C71-C70-C73	121.3(2)	Cl3-C1A-Cl1	109.6(5)
C69-C70-C73	120.4(2)	Cl2-C1A-H1AA	107.8
C72-C71-C70	121.5(2)	Cl3-C1A-H1AA	107.8
C72-C71-H71	119.2	Cl1-C1A-H1AA	107.8
C70-C71-H71	119.2	C2B-C1B-H1B1	109.5
C71-C72-C67	121.0(3)	C2B-C1B-H1B2	109.5
C71-C72-H72	119.5	H1B1-C1B-H1B2	109.5
C67-C72-H72	119.5	C2B-C1B-H1B3	109.5
C78-C73-C74	118.3(2)	H1B1-C1B-H1B3	109.5
C78-C73-C70	118.1(2)	H1B2-C1B-H1B3	109.5
C74-C73-C70	123.5(2)	C3B-C2B-C1B	114.8(8)
C75-C74-C73	118.7(2)	C3B-C2B-H2B1	108.6
C75-C74-C83	116.8(2)	C1B-C2B-H2B1	108.6
C73-C74-C83	124.4(2)	C3B-C2B-H2B2	108.6
C76-C75-C74	121.8(3)	C1B-C2B-H2B2	108.6
C76-C75-H75	119.1	H2B1-C2B-H2B2	107.6
C74-C75-H75	119.1	C2B-C3B-C4B	110.1(8)
C75-C76-C77	119.4(3)	C2B-C3B-H3B1	109.6
C75-C76-H76	120.3	C4B-C3B-H3B1	109.6
C77-C76-H76	120.3	C2B-C3B-H3B2	109.6
C78-C77-C76	119.6(3)	C4B-C3B-H3B2	109.6
C78-C77-H77	120.2	H3B1-C3B-H3B2	108.2
C76-C77-H77	120.2	C5B-C4B-C3B	113.4(8)
C77-C78-C73	122.1(3)	C5B-C4B-H4B1	108.9
C77-C78-H78	118.9	C3B-C4B-H4B1	108.9
C73-C78-H78	118.9	C5B-C4B-H4B2	108.9

C3B-C4B-H4B2	108.9	H5B1-C5B-H5B2	109.5
H4B1-C4B-H4B2	107.7	C4B-C5B-H5B3	109.5
C4B-C5B-H5B1	109.5	H5B1-C5B-H5B3	109.5
C4B-C5B-H5B2	109.5	H5B2-C5B-H5B3	109.5

Table 6.6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6.6a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	17(1)	26(1)	23(1)	0(1)	6(1)	0(1)
C2	17(1)	25(1)	23(1)	5(1)	7(1)	2(1)
C3	13(1)	25(1)	22(1)	1(1)	3(1)	-1(1)
C4	20(1)	22(1)	23(1)	0(1)	4(1)	-1(1)
C5	16(1)	28(1)	24(1)	5(1)	5(1)	-1(1)
C6	19(1)	29(1)	19(1)	-1(1)	6(1)	-2(1)
C7	23(1)	25(1)	21(1)	1(1)	7(1)	3(1)
C8	26(1)	31(2)	29(2)	2(1)	13(1)	1(1)
C9	33(2)	33(2)	33(2)	-1(1)	17(1)	6(1)
C10	38(2)	26(1)	34(2)	-2(1)	14(1)	4(1)
C11	32(2)	25(1)	34(2)	-6(1)	10(1)	-1(1)
C12	23(1)	27(1)	24(1)	-1(1)	5(1)	3(1)
C13	22(1)	25(1)	26(1)	-4(1)	6(1)	-2(1)
C14	27(1)	21(1)	35(2)	0(1)	9(1)	1(1)
C15	24(1)	25(1)	31(2)	1(1)	8(1)	-4(1)
C16	24(1)	24(1)	23(1)	-1(1)	5(1)	0(1)
C17	24(1)	22(1)	27(1)	1(1)	6(1)	1(1)
C18	23(1)	24(1)	31(2)	1(1)	9(1)	-1(1)
C19	21(1)	24(1)	23(1)	0(1)	4(1)	0(1)
C20	27(1)	20(1)	26(1)	2(1)	8(1)	0(1)
C21	24(1)	24(1)	28(1)	4(1)	8(1)	-4(1)
C22	20(1)	27(1)	18(1)	1(1)	2(1)	-3(1)
C23	22(1)	21(1)	31(2)	-1(1)	5(1)	-1(1)
C24	19(1)	24(1)	39(2)	1(1)	7(1)	-5(1)
C25	23(1)	28(1)	20(1)	-3(1)	7(1)	-5(1)
C26	33(2)	33(2)	28(2)	2(1)	10(1)	-1(1)
C27	37(2)	48(2)	29(2)	5(1)	16(1)	-6(1)
C28	26(2)	50(2)	33(2)	-1(1)	15(1)	-3(1)
C29	18(1)	37(2)	28(2)	1(1)	7(1)	-1(1)
C30	21(1)	27(1)	20(1)	-2(1)	5(1)	-4(1)
C31	18(1)	25(1)	21(1)	1(1)	7(1)	-3(1)
C32	18(1)	29(1)	25(1)	0(1)	8(1)	1(1)
C33	15(1)	33(2)	22(1)	2(1)	1(1)	0(1)
C34	20(1)	37(2)	19(1)	-3(1)	4(1)	-3(1)
C35	18(1)	28(1)	25(1)	-4(1)	6(1)	-1(1)
C36	16(1)	23(1)	24(1)	1(1)	3(1)	-1(1)
C37	20(1)	28(1)	22(1)	0(1)	2(1)	2(1)
C38	20(1)	24(1)	27(1)	-3(1)	4(1)	4(1)
C39	19(1)	27(1)	27(1)	-5(1)	3(1)	-2(1)
C40	21(1)	30(2)	29(2)	-4(1)	-5(1)	4(1)
C41	34(2)	28(2)	51(2)	-9(1)	-9(1)	8(1)

C42	29(2)	28(2)	45(2)	-8(1)	-9(1)	1(1)
C43	27(1)	27(1)	31(2)	-6(1)	-3(1)	7(1)
C44	24(1)	30(2)	35(2)	0(1)	5(1)	4(1)
C45	23(1)	32(2)	30(2)	-2(1)	2(1)	0(1)
C46	20(1)	26(1)	32(2)	-4(1)	1(1)	3(1)
C47	29(2)	41(2)	44(2)	-11(2)	5(1)	10(1)
C48	31(2)	45(2)	40(2)	-13(2)	-1(1)	5(1)
C49	17(1)	27(1)	28(1)	-2(1)	5(1)	2(1)
C50	18(1)	24(1)	26(1)	1(1)	7(1)	1(1)
C51	18(1)	25(1)	31(2)	-2(1)	1(1)	0(1)
C52	19(1)	28(2)	35(2)	1(1)	1(1)	6(1)
C53	23(1)	22(1)	41(2)	-2(1)	9(1)	4(1)
C54	20(1)	24(1)	35(2)	-6(1)	5(1)	2(1)
C55	27(1)	21(1)	23(1)	2(1)	9(1)	-1(1)
C56	27(1)	34(2)	23(1)	3(1)	5(1)	-4(1)
C57	34(2)	40(2)	35(2)	6(1)	9(1)	-12(1)
C58	40(2)	37(2)	36(2)	12(1)	13(1)	-8(1)
C59	31(2)	37(2)	29(2)	11(1)	8(1)	1(1)
C60	25(1)	28(1)	29(2)	4(1)	10(1)	2(1)
C61	21(1)	29(1)	25(1)	6(1)	7(1)	4(1)
C62	25(1)	46(2)	22(1)	4(1)	7(1)	1(1)
C63	26(1)	49(2)	26(2)	6(1)	12(1)	2(1)
C64	20(1)	34(2)	26(1)	6(1)	6(1)	5(1)
C65	25(1)	40(2)	23(1)	4(1)	8(1)	2(1)
C66	24(1)	36(2)	25(1)	7(1)	10(1)	2(1)
C67	22(1)	37(2)	26(1)	2(1)	10(1)	3(1)
C68	22(1)	49(2)	23(1)	8(1)	4(1)	4(1)
C69	24(1)	41(2)	26(1)	6(1)	10(1)	2(1)
C70	24(1)	27(1)	23(1)	-1(1)	9(1)	3(1)
C71	26(1)	34(2)	21(1)	0(1)	5(1)	3(1)
C72	30(1)	34(2)	24(1)	4(1)	11(1)	1(1)
C73	24(1)	24(1)	22(1)	3(1)	4(1)	3(1)
C74	21(1)	22(1)	21(1)	2(1)	3(1)	2(1)
C75	24(1)	30(2)	28(2)	-3(1)	4(1)	-1(1)
C76	30(2)	30(2)	31(2)	-4(1)	-1(1)	-6(1)
C77	38(2)	29(2)	24(2)	-5(1)	1(1)	2(1)
C78	33(2)	34(2)	23(1)	-1(1)	8(1)	6(1)
C79	11(1)	26(1)	24(1)	1(1)	2(1)	-1(1)
C80	14(1)	26(1)	23(1)	-3(1)	3(1)	1(1)
C81	10(1)	24(1)	27(1)	0(1)	2(1)	1(1)
C82	16(1)	27(1)	24(1)	3(1)	6(1)	0(1)
C83	14(1)	25(1)	25(1)	0(1)	4(1)	0(1)
C84	16(1)	24(1)	25(1)	1(1)	5(1)	0(1)
Cl1	101(2)	36(1)	74(2)	-5(1)	39(2)	-11(1)
Cl2	122(4)	111(4)	157(5)	-64(4)	81(3)	-27(3)
Cl3	191(4)	43(2)	64(2)	-13(1)	77(2)	-26(2)

C1A	105(5)	91(5)	79(5)	-7(4)	59(4)	-25(5)
C1B	132(6)	151(7)	96(5)	-25(5)	41(5)	20(6)
C2B	102(5)	104(5)	95(5)	-14(4)	42(4)	-7(4)
C3B	111(4)	119(4)	89(4)	-36(4)	46(4)	-28(4)
C4B	113(5)	100(5)	105(5)	-68(4)	64(4)	-19(4)
C5B	96(5)	74(4)	79(5)	-7(4)	52(4)	17(4)

Table 6.7. Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **6.6a**.

	x	y	z	U(eq)
H2	7434	1148	5077	26
H4	7694	3241	4708	27
H6	7255	1809	3124	27
H8	8390	710	3663	33
H9	8522	-464	3343	38
H10	7499	-1292	3298	39
H11	6353	-938	3545	37
H14	5716	-686	4276	34
H15	4437	-465	4350	32
H17	4505	1534	3622	30
H18	5773	1310	3538	31
H20	3131	-288	4145	30
H21	1886	-7	4255	31
H23	2337	2086	4102	31
H24	3582	1805	4000	34
H26	1325	549	5089	38
H27	160	866	5344	44
H28	-686	1783	4715	42
H29	-375	2360	3811	34
H32	8815	1826	6104	28
H33	9211	2139	7289	30
H34	8384	2902	7673	31
H35	7175	3346	6866	29
H38	6035	2132	5035	29
H39	4701	2464	4432	31
H41	5158	4434	5268	53
H42	6501	4106	5874	47
H44	3736	3010	3571	37
H45	2423	3366	2898	36
H47	2431	4770	4412	48
H48	3751	4409	5087	50
H51	-230	4090	1856	32
H52	-290	5322	1732	36
H53	780	6024	2467	35
H54	1887	5482	3318	33
H56	8764	3414	4028	35
H57	9066	4297	3339	44
H58	8078	4632	2271	45
H59	6797	4089	1907	39
H62	5949	3155	3418	37

H63	4598	2790	2993	39
H65	4708	2601	1039	35
H66	6051	2989	1456	34
H68	3627	2002	2640	39
H69	2277	1626	2271	36
H71	1943	2413	329	33
H72	3298	2785	697	35
H75	-537	1360	1371	35
H76	-905	723	321	40
H77	-16	693	-328	40
H78	1236	1269	96	36
H80	863	3157	3664	26
H82	838	3087	1653	27
H84	711	1260	2671	27
H1AA	4984	5048	2467	102
H1B1	4249	5891	3309	189
H1B2	3652	5226	3018	189
H1B3	4020	5648	2506	189
H2B1	4825	4689	3586	118
H2B2	4803	4678	2790	118
H3B1	5677	5726	3768	124
H3B2	5727	5594	3001	124
H4B1	6285	4604	4153	119
H4B2	6282	4423	3380	119
H5B1	7121	5557	3629	116
H5B2	7512	4776	3782	116
H5B3	7370	5225	4403	116

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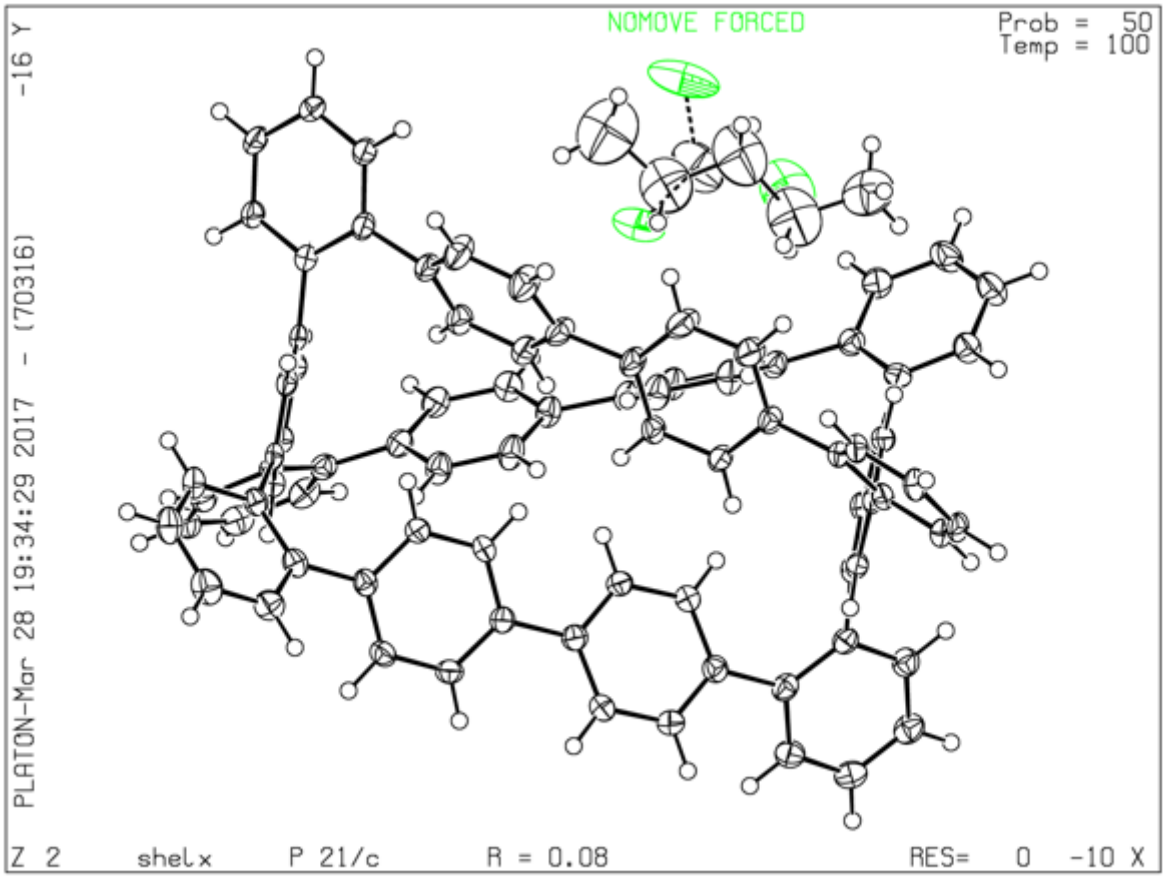
Table 6.8. Torsion angles [°] for **6.6a**.

C6-C1-C2-C3	-0.2(4)	C17-C16-C19-C24	-16.3(4)
C7-C1-C2-C3	171.6(2)	C24-C19-C20-C21	0.3(4)
C1-C2-C3-C4	-0.7(4)	C16-C19-C20-C21	179.1(2)
C1-C2-C3-C31	-176.0(2)	C19-C20-C21-C22	0.3(4)
C2-C3-C4-C5	0.6(4)	C20-C21-C22-C23	-0.8(4)
C31-C3-C4-C5	176.0(2)	C20-C21-C22-C25	-176.7(2)
C3-C4-C5-C6	0.5(4)	C21-C22-C23-C24	0.5(4)
C3-C4-C5-C55	-173.9(2)	C25-C22-C23-C24	176.6(2)
C2-C1-C6-C5	1.4(4)	C22-C23-C24-C19	0.1(4)
C7-C1-C6-C5	-170.5(2)	C20-C19-C24-C23	-0.6(4)
C4-C5-C6-C1	-1.5(4)	C16-C19-C24-C23	-179.3(2)
C55-C5-C6-C1	172.8(2)	C23-C22-C25-C30	44.8(4)
C6-C1-C7-C8	62.4(3)	C21-C22-C25-C30	-139.3(3)
C2-C1-C7-C8	-109.4(3)	C23-C22-C25-C26	-132.6(3)
C6-C1-C7-C12	-119.9(3)	C21-C22-C25-C26	43.2(4)
C2-C1-C7-C12	68.3(3)	C30-C25-C26-C27	-1.9(4)
C12-C7-C8-C9	-1.5(4)	C22-C25-C26-C27	175.6(3)
C1-C7-C8-C9	176.4(2)	C25-C26-C27-C28	-0.4(5)
C7-C8-C9-C10	0.6(4)	C26-C27-C28-C29	1.1(5)
C8-C9-C10-C11	0.8(4)	C27-C28-C29-C30	0.5(4)
C9-C10-C11-C12	-1.3(4)	C28-C29-C30-C25	-2.8(4)
C10-C11-C12-C7	0.4(4)	C28-C29-C30-C79	175.3(2)
C10-C11-C12-C13	176.7(3)	C26-C25-C30-C29	3.5(4)
C8-C7-C12-C11	0.9(4)	C22-C25-C30-C29	-174.0(2)
C1-C7-C12-C11	-176.7(2)	C26-C25-C30-C79	-174.5(2)
C8-C7-C12-C13	-175.1(2)	C22-C25-C30-C79	8.0(4)
C1-C7-C12-C13	7.3(4)	C2-C3-C31-C32	64.5(3)
C11-C12-C13-C14	31.2(4)	C4-C3-C31-C32	-110.9(3)
C7-C12-C13-C14	-152.8(3)	C2-C3-C31-C36	-119.3(3)
C11-C12-C13-C18	-142.8(3)	C4-C3-C31-C36	65.4(3)
C7-C12-C13-C18	33.3(4)	C36-C31-C32-C33	-1.4(4)
C18-C13-C14-C15	0.6(4)	C3-C31-C32-C33	175.0(2)
C12-C13-C14-C15	-173.7(2)	C31-C32-C33-C34	0.0(4)
C13-C14-C15-C16	-0.6(4)	C32-C33-C34-C35	0.2(4)
C14-C15-C16-C17	0.1(4)	C33-C34-C35-C36	1.1(4)
C14-C15-C16-C19	-178.5(2)	C34-C35-C36-C31	-2.5(4)
C15-C16-C17-C18	0.3(4)	C34-C35-C36-C37	173.6(2)
C19-C16-C17-C18	178.9(2)	C32-C31-C36-C35	2.6(4)
C16-C17-C18-C13	-0.2(4)	C3-C31-C36-C35	-173.7(2)
C14-C13-C18-C17	-0.2(4)	C32-C31-C36-C37	-173.3(2)
C12-C13-C18-C17	174.0(2)	C3-C31-C36-C37	10.4(4)
C15-C16-C19-C20	-16.3(4)	C35-C36-C37-C42	41.6(4)
C17-C16-C19-C20	165.1(3)	C31-C36-C37-C42	-142.5(3)
C15-C16-C19-C24	162.3(3)	C35-C36-C37-C38	-130.1(3)

C31-C36-C37-C38	45.8(4)	C55-C56-C57-C58	0.8(5)
C42-C37-C38-C39	-0.8(4)	C56-C57-C58-C59	0.4(5)
C36-C37-C38-C39	171.3(3)	C57-C58-C59-C60	-0.7(5)
C37-C38-C39-C40	0.5(4)	C58-C59-C60-C55	0.0(4)
C38-C39-C40-C41	-0.2(5)	C58-C59-C60-C61	176.8(3)
C38-C39-C40-C43	-179.8(3)	C56-C55-C60-C59	1.1(4)
C39-C40-C41-C42	0.3(5)	C5-C55-C60-C59	-177.7(3)
C43-C40-C41-C42	179.9(3)	C56-C55-C60-C61	-175.5(3)
C40-C41-C42-C37	-0.6(6)	C5-C55-C60-C61	5.7(4)
C38-C37-C42-C41	0.8(5)	C59-C60-C61-C66	44.0(4)
C36-C37-C42-C41	-171.2(3)	C55-C60-C61-C66	-139.3(3)
C41-C40-C43-C44	149.9(3)	C59-C60-C61-C62	-131.1(3)
C39-C40-C43-C44	-30.5(5)	C55-C60-C61-C62	45.6(4)
C41-C40-C43-C48	-29.5(5)	C66-C61-C62-C63	-0.6(4)
C39-C40-C43-C48	150.1(3)	C60-C61-C62-C63	174.6(3)
C48-C43-C44-C45	4.2(5)	C61-C62-C63-C64	0.4(5)
C40-C43-C44-C45	-175.3(3)	C62-C63-C64-C65	0.5(4)
C43-C44-C45-C46	0.8(5)	C62-C63-C64-C67	-179.8(3)
C44-C45-C46-C47	-5.8(4)	C63-C64-C65-C66	-1.3(4)
C44-C45-C46-C49	170.5(3)	C67-C64-C65-C66	179.0(3)
C45-C46-C47-C48	5.8(5)	C64-C65-C66-C61	1.1(4)
C49-C46-C47-C48	-170.5(3)	C62-C61-C66-C65	-0.1(4)
C46-C47-C48-C43	-0.8(5)	C60-C61-C66-C65	-175.4(3)
C44-C43-C48-C47	-4.2(5)	C63-C64-C67-C72	151.5(3)
C40-C43-C48-C47	175.2(3)	C65-C64-C67-C72	-28.9(4)
C47-C46-C49-C54	45.5(4)	C63-C64-C67-C68	-27.4(4)
C45-C46-C49-C54	-130.7(3)	C65-C64-C67-C68	152.2(3)
C47-C46-C49-C50	-141.6(3)	C72-C67-C68-C69	1.0(4)
C45-C46-C49-C50	42.2(4)	C64-C67-C68-C69	179.9(3)
C54-C49-C50-C51	0.4(4)	C67-C68-C69-C70	-0.3(5)
C46-C49-C50-C51	-172.4(3)	C68-C69-C70-C71	-0.6(4)
C54-C49-C50-C81	-179.6(3)	C68-C69-C70-C73	173.5(3)
C46-C49-C50-C81	7.5(4)	C69-C70-C71-C72	0.7(4)
C49-C50-C51-C52	1.2(4)	C73-C70-C71-C72	-173.3(3)
C81-C50-C51-C52	-178.8(3)	C70-C71-C72-C67	-0.1(4)
C50-C51-C52-C53	-1.3(5)	C68-C67-C72-C71	-0.8(4)
C51-C52-C53-C54	-0.1(4)	C64-C67-C72-C71	-179.7(3)
C52-C53-C54-C49	1.8(4)	C71-C70-C73-C78	43.6(4)
C50-C49-C54-C53	-1.9(4)	C69-C70-C73-C78	-130.3(3)
C46-C49-C54-C53	171.4(3)	C71-C70-C73-C74	-141.2(3)
C4-C5-C55-C56	57.2(3)	C69-C70-C73-C74	45.0(4)
C6-C5-C55-C56	-117.1(3)	C78-C73-C74-C75	0.1(4)
C4-C5-C55-C60	-124.0(3)	C70-C73-C74-C75	-175.2(2)
C6-C5-C55-C60	61.8(4)	C78-C73-C74-C83	-176.7(2)
C60-C55-C56-C57	-1.5(4)	C70-C73-C74-C83	8.0(4)
C5-C55-C56-C57	177.4(3)	C73-C74-C75-C76	0.5(4)

C83-C74-C75-C76	177.6(2)
C74-C75-C76-C77	-1.0(4)
C75-C76-C77-C78	0.8(4)
C76-C77-C78-C73	-0.3(4)
C74-C73-C78-C77	-0.2(4)
C70-C73-C78-C77	175.3(3)
C29-C30-C79-C80	58.8(3)
C25-C30-C79-C80	-123.1(3)
C29-C30-C79-C84	-115.9(3)
C25-C30-C79-C84	62.1(3)
C84-C79-C80-C81	0.6(4)
C30-C79-C80-C81	-174.4(2)
C79-C80-C81-C82	0.8(4)
C79-C80-C81-C50	175.2(2)
C51-C50-C81-C80	-115.2(3)
C49-C50-C81-C80	64.9(4)
C51-C50-C81-C82	59.2(3)
C49-C50-C81-C82	-120.7(3)
C80-C81-C82-C83	-0.3(4)
C50-C81-C82-C83	-174.7(2)
C81-C82-C83-C84	-1.6(4)
C81-C82-C83-C74	172.3(2)
C75-C74-C83-C82	-114.5(3)
C73-C74-C83-C82	62.4(3)
C75-C74-C83-C84	59.3(3)
C73-C74-C83-C84	-123.8(3)
C82-C83-C84-C79	3.1(4)
C74-C83-C84-C79	-170.9(2)
C80-C79-C84-C83	-2.6(4)
C30-C79-C84-C83	172.3(2)
C1B-C2B-C3B-C4B	170.8(8)
C2B-C3B-C4B-C5B	175.4(8)

Figure 6.4. View of **6.6a** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Chapter 7. Alternating oligo(*o,p*-Phenylenes) *via* Ruthenium Catalyzed Diol-Diene Benzannulation: Orthogonality to Cross-Coupling Enables *De Novo* PAH Construction*

7.1 Introduction

Oligophenylenes, whose structures are composed of conjugated phenylene chains are important class of polycyclic aromatic hydrocarbons (PAHs). Many scientists have investigated oligophenylenes because of their tunable physical properties are promising candidates for organic photovoltaic materials.[1] Additionally, oligophenylenes are useful scaffold to access other important PAHs classes. For example, Scholl oxidation[2–4] of oligophenylene leads to helicenes and nanographene materials.[5,6] Despite the longstanding importance of oligophenylenes and nanographenes, the number of synthetic methodologies are unreasonably small compared to the huge number of the reported oligophenylenes. Cross-coupling[7] followed by Scholl oxidation[2–4] or palladium catalyzed cyclo-dehydrohalogenations[8–10] are among the most powerful synthetic methodologies for oligophenylene synthesis. While many other benzannulation protocols have been reported,[11] development of new catalytic methods that are orthogonal to biaryl cross-coupling would expand PAHs chemical space. In the course of the development of alcohol-mediated carbonyl addition reactions,[12] our group discovered a ruthenium(0) catalyzed diene–diol [4+2] cycloaddition reactions (Scheme 7.1).[12e,13a,b] Dehydration of hexene diol cycloadduct with acid

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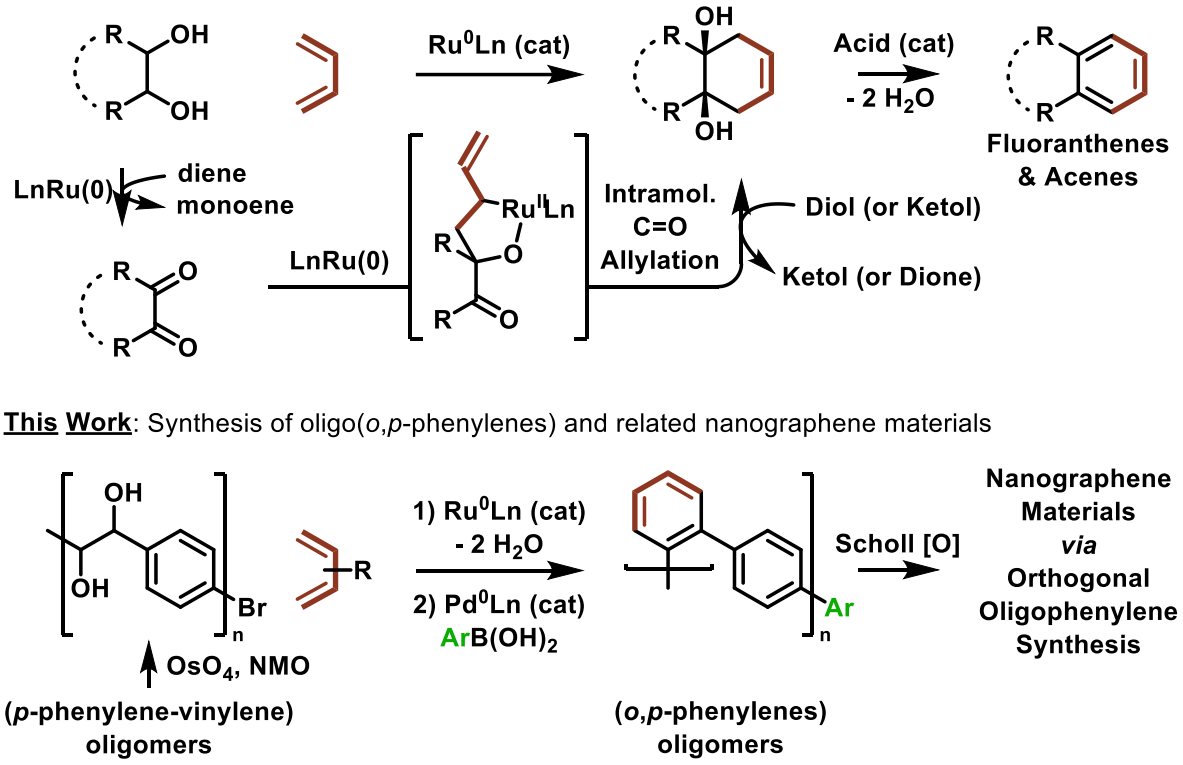
This chapter is based on the published work:

* Kasun, Z. A.; Sato, H.; Nie, J.; Mori, Y.; Bender, J. A.; Roberts, S. T.; Krische, M. J. *Chem. Sci*, **2018**, *9*, 7866.

Contribution of HS: The main ideas of applying the cycloaddition to diverse PAHs were invented by HS. The initial results and most of the substrates in this thesis were done by HS. Applications to helicene, HBC, and nanographene were also invented by HS, and HBCs were synthesized by HS.

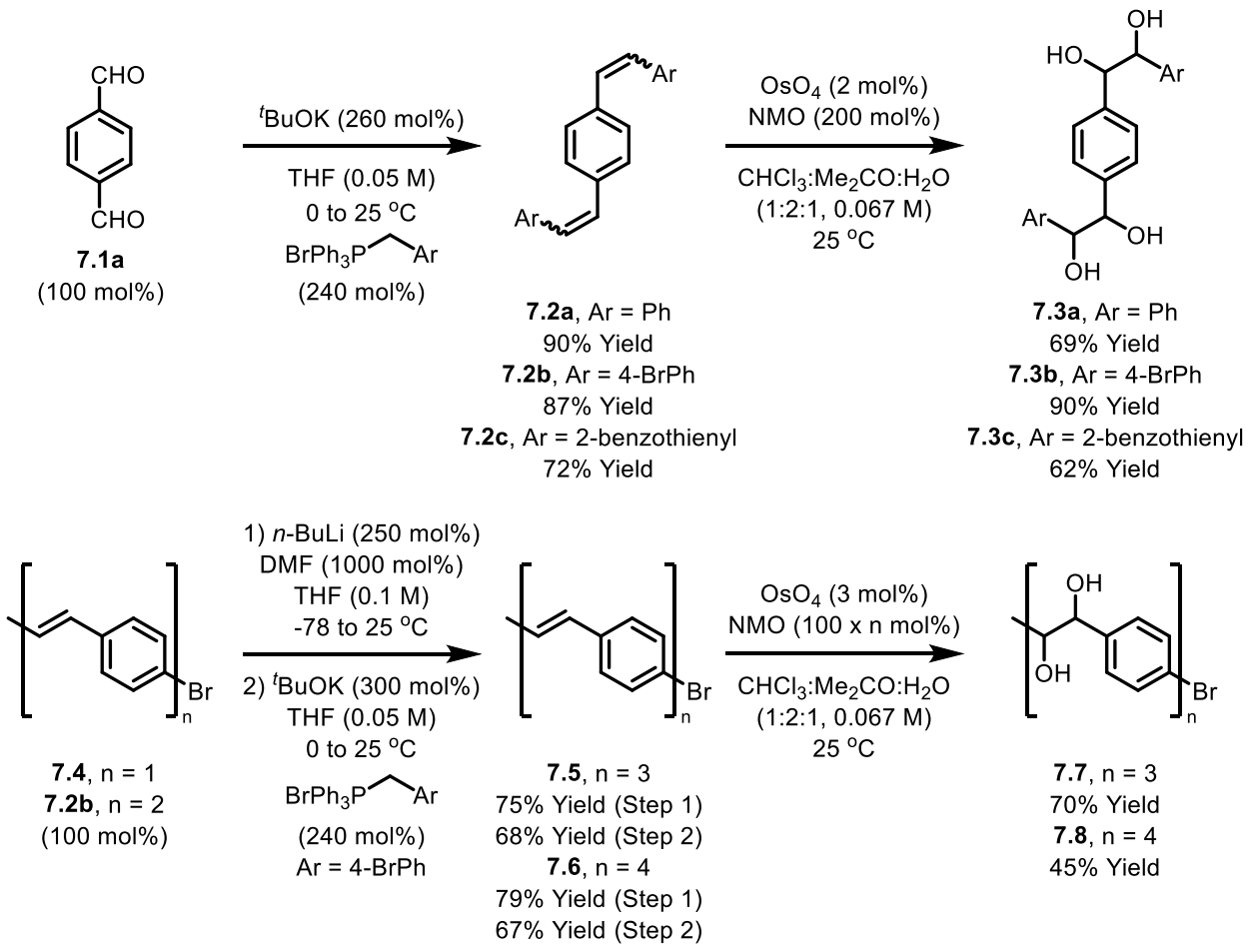


Scheme 7.1. Alternating *o,p*-oligophenylenes and nanogra-phenes via ruthenium catalyzed diol-diene benzannulation.

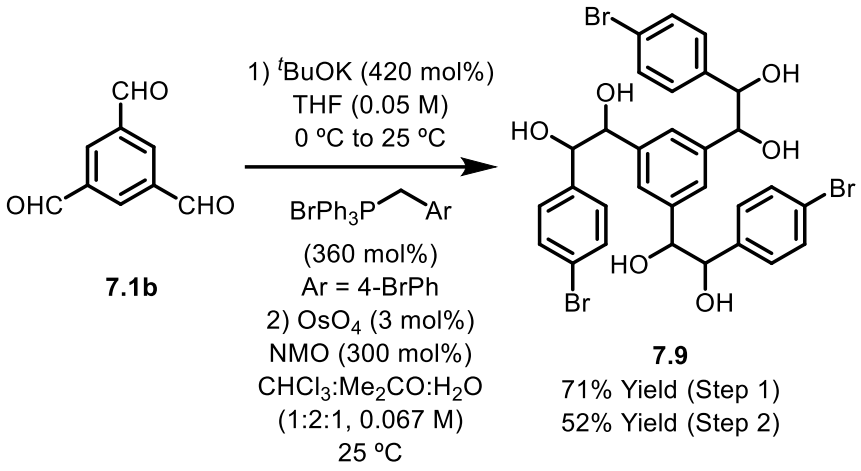
gives the corresponding aromatized compounds acenes.[13c] Because this method tolerates aryl halide after the reactions, the products bearing aryl bromide are further functionalized by conventional cross coupling reactions. In an initial application of this method, triple-stranded phenylene cages were prepared.[13d,14] This demonstration proved the feasibility of PAHs syntheses wherein diol–diene benzannulation is used to generate bromide-containing oligophenylenes amenable to diversification by coupling reactions. Herein, as another application of this orthogonal method, we will present the syntheses of various alternating oligo(*o,p*-phenylenes)[15] via ruthenium(0) catalyzed diol–diene benzannulation and, the diversification to S-doped helicene and nanographenes.

7.2 Results and Discussion

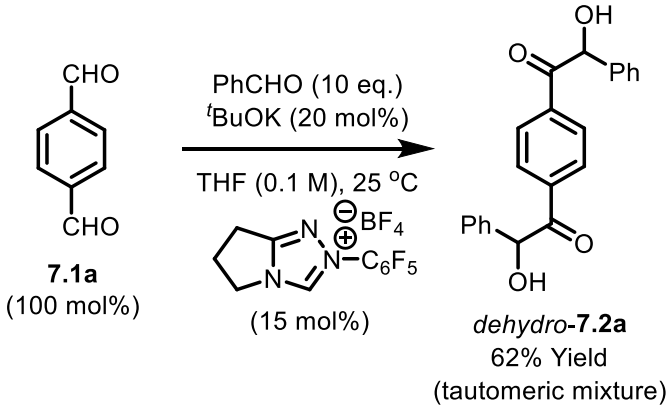
The synthesis of the oligo(p-phenylenevinylene) diols **7.3a–c** is readily accomplished through Wittig olefination (Scheme 7.2).[16,17] Thus, following the precedenece, [17d] terephthaladehyde **7.1a** was reacted with the phosphonium salts in the presence of *t*-BuOK to give the respective oligo(*p*-phenylene vinylenes) **7.2a–c** in good yields. Other bases such as KOH, NaOH, NaOtBu, nBuLi and lithium diisopropylamide (LDA) insead of *t*-BuOK resulted in poor yields. The reaction with other olefination source, Horner–Wadsworth–Emmons (HWE) reagents



Scheme 7.2. Synthesis of oligo(*p*-phenylene vinylene) diols **7.3a**-**7.3c**, **7.7** and **7.8**.



Scheme 7.3. Synthesis of tris-diol **7.9** from trialdehyde **7.1b**.



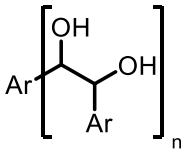
Scheme 7.4. Synthesis of dehydro-**7.2a** from dialdehyde **7.1a** via cross benzoin.

resulted in lower yield with the homocoupling byproducts.[18] Upjohn dihydroxylation conditions using N-methylmorpholine N-oxide (NMO)[20] was efficient to deliver the oligo(p-phenylene vinylene) diols **7.3a–c** avoiding oxidative cleavage to form aldehyde byproducts.[19] In a similar manner, a three-directional synthesis of trisdiol[9] was accomplished from benzene-1,3,5-tricarbaldehyde **7.1b** (Scheme 7.3).[13d] The longer oligo(p-phenylene vinylene) diols **7.7** and **7.8** was prepared in similar manners as shown in scheme 7.2. Thus, lithiation of **7.4** and **7.2b** with n-BuLi followed by treatment with DMF provided the respective formyl derivatives,[21] which upon Wittig olefination to give oligo(*p*-phenylene vinylenes) **7.5** and **7.6** with bromide at the terminus.

Following dihydroxylation reactions of the oligo(*p*-phenylene vinylenes) **7.5** and **7.6** to furnish the oligo(*p*-phenylene vinylene) diols **7.7** and **7.8**. As the ruthenium(0) catalyzed [4 + 2] cycloaddition can beconducted from the ketol oxidation level,[12e,13] preparation for the ketol was also examined. The crossed-benzoin condensation of terephthaladehyde **7.1a** with excess amount of benzaldehyde with an N-heterocyclic carbene (NHC) catalyst gave ketol dehydro-**7.3a** in good yield (Scheme 7.4).[22] However, these conditions were quite substrate dependent. The ractions of 4-bromo benzaldehyde and 2-benzothiophene carboxaldehyde was ineffective due to competing homo-benzoin condensations. The starting substrates oligo(*p*-phenylene vinylene) diols **7.3a–c** in hand, ruthenium catalyzed cycloaddition reactions and dehydration reactions were explored (Table 1). To our delight, the reactions of oligo(*p*-phenylene vinylene) diols **7.3a–c**, **7.7–7.9** with 1,3-butadiene using a catalytic amount of $Ru_3(CO)_{12}$ and 3,5-dimethyl benzoic acid (3,5-Me_2BzOH) afforded the corresponding cyclohexene diols in good yield in the mixture of stereoisomers.[12e,13] Subsequent exposure of the cycloadducts to substoichiometric amount of *p*-toluenesulfonic acid (*p*-TsOH) resulted in dehydration to form the alternating oligo(*o,p*-phenylenes) **7.10a–c**, **7.11–7.13** in moderate to good yields.[13c]

The alternating oligo(*o,p*-phenylenes) **7.10a–c**, **7.11–7.13** prepared by our methods are good scaffolds to access other important PAHs compounds, including helicenes and graphene nanodots. For example, the treatment of oligo(*o,p*-phenylenes) **7.10c** with $FeCl_3$ under Scholl oxidation conditions provided the corresponding S-doped helical picene derivative **7.14**, which was characterized by single crystal X-ray diffraction (Scheme 7.5).[23] The regioisomeric compound iso-**7.14** was not observed. The outcome of complete regioselectivity is consistent with the work reported by Hilt and co-workers.[24] Another demonstration for diversification is the synthesis for hexa-*peri*-hexabenzocoronenes (HBCs), which is a unique PAH class as the smallest benzenoid

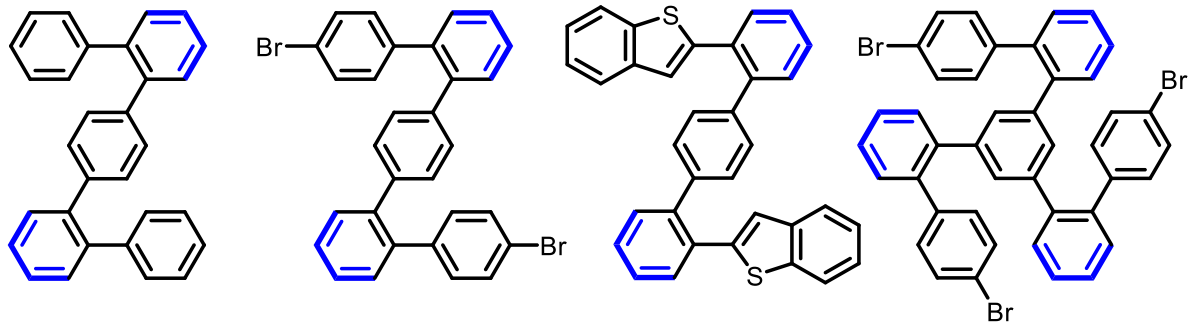
Table 7.1. Ruthenium(0) catalyzed benzannulation of oligo(*p*-phenylene vinylene) diols **7.3a-7.3c**, **7.7-7.9** to form alternat-ing oligo(o,p-phenylenes) **7.10a-c**, **7.11-7.13**.[a]



7.3a-c, **7.7-7.9** (100 mol%)

1) Ru_3CO_{12} (2n mol%)
dppp (6n mol%)
3,5-Me_2BzOH (10 mol%)
(500n mol%)

PhMe:DMAc (1:1)
130 °C - 140 °C
2) *p*-TsOH (10 mol%)
PhMe, 60-85 °C

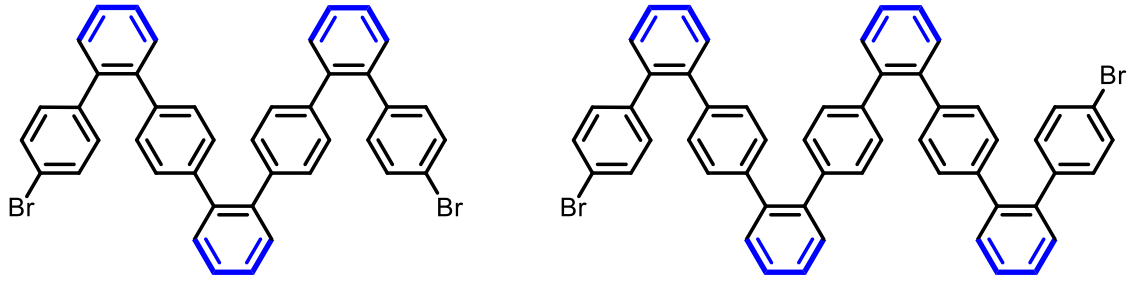


7.10a, n=2
82% Yield (Step 1)
79% Yield (Step 1)[b]
75% Yield (Step 2)

7.10b, n=2
88% Yield (Step 1)
86% Yield (Step 2)

7.10c, n=2
79% Yield (Step 1)
73% Yield (Step 2)

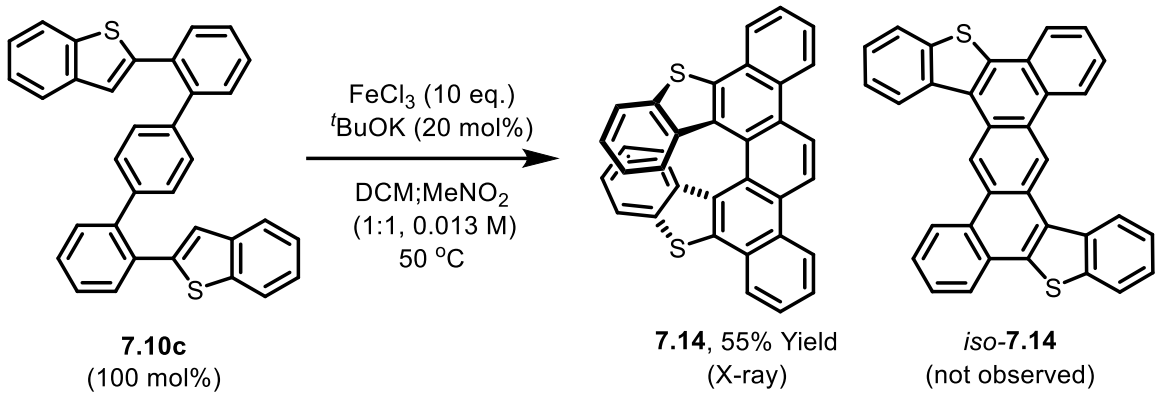
7.13, n=3
81% Yield (Step 1)
90% Yield (Step 2)



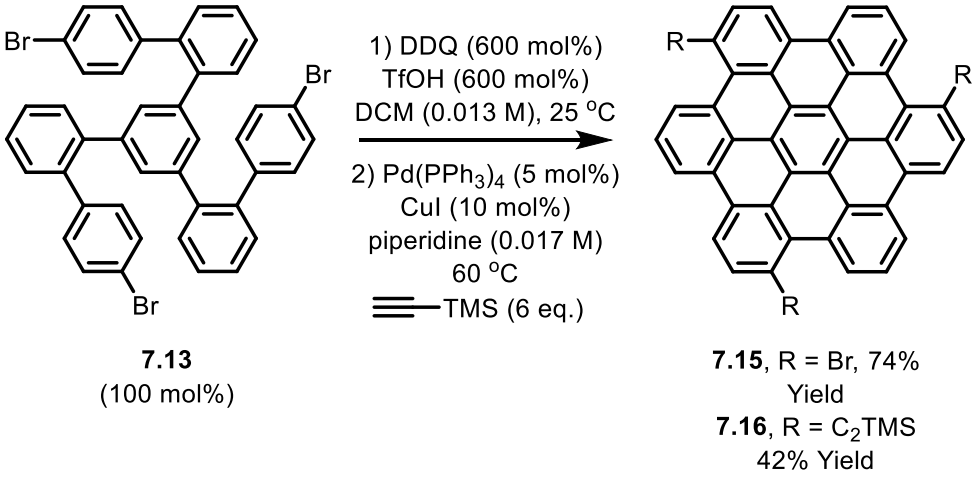
7.11, n=3 (X-ray)
91% Yield (Step 1)
64% Yield (Step 2)

7.12, n=4
65% Yield (Step 1)
51% Yield (Step 2)

[a]Yields are of material isolated by silica gel chromatography. [b]Yield from dehydro-**7.2a**. See Supporting Information for further experi-mental details



Scheme 7.5. Synthesis of S-doped helicene **7.14** from **7.10c** by Scholl oxidation.



Scheme 7.6. Synthesis of HBCs **7.15** and **7.16** from heptaphenylene **7.13**.

showing intriguing *opto*-electronic properties.[6] While HBCs have been intensively studied by Müllen and the coworkers, syntheses of HBCs with low symmetry[25] or electron deficient substituent groups or those substituted at the bay region remain elusive.[26] The synthesis of the electron deficient D_3h symmetric HBC **7.17**, bearing bromo in the bay region, was achieved through Scholl oxidation of the branched 3-fold heptaphenylene [13] under modified Scholl oxidation condition with DDQ and triflic acid (Scheme 7.6).[27] Although the resulting HBC **7.15** is quite insoluble, conventional cross coupling reactions were able to further functionalize the bromide moiety to explore soluble analogues. Sonogashira coupling[28] between HBC **7.15** and

trimethylsilylacetylene occurred in good yield to furnish the chloroform-soluble **7.16**, which was characterize by 1H and 13C NMR and MALDI-TOF mass spectrometry.

7.3 Summary

In summary, we report the synthesis of oligophenylenes and PAH derivatives utilizing Ru(0) catalyzed diol cycloaddition reactions.[4] Those oligophenylenes are diversified by Scholl oxidation and Pd cross coupling reactions to give benzothiophene helical picene **7.14** and hexa-peri-hexabenzocoronene **7.16**. Future studies will focus on the development of related methods for alcohol-mediated benzannulation and their application to PAH construction, including the use of symmetric 2,3-diaryl-substituted butadiene building blocks.

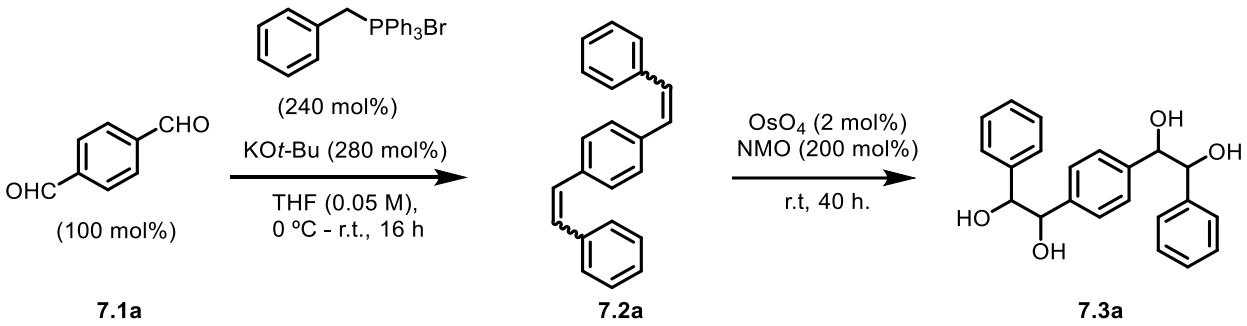
7.4 Experimental Details

General Comments

All glassware was oven dried at 120 °C overnight and cooled in a desiccator. All ruthenium catalyzed reactions were carried in sealed pressure tubes (13 x 100 mm). THF was purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], dppp, 3,5-dimethylbenzoic acid were purchased from commercial suppliers and used as received. Aldehyde **7.1a** was purchased from commercially available sources and used without purification. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with a Varian Gemini spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on a Karatos MS9 and are reported as m/z. Mass spectra (MS) were obtained on a Water Micromass AutoSpec Ultima (HR-CI), Agilent Technologies 6530 Accurate Mas Q-TOF (HR-ESI, HR-APCI, HR-APPI), and Applied Biosystems Voyager DE-Pro (MALDI-TOF, 337nm N2 laser, 3 ns pulse, 20,000 kV source) are reported as m/z. Masses are reported for the molecular ion (M-H, M, M+H, M+Na, M+K, or other suitable adduct, as noted). Tetracyanoquinodimethane (TCNQ) was used as a matrix in MALDI-TOF experiments.

Synthesis of Starting Materials

2,2'-(1,4-phenylene)bis(1-phenylethane-1,2-diol) (7.3a)



7.1a **7.2a** **7.3a**

<u>1,4-distyrylbenzene (**7.2a**):</u>

To a solution of KO*t*-Bu (1.12 g, 28.0 mmol, 280 mol%) in anhydrous THF (100 mL) cooled to 0 ˚C was added phosphonium salt (10.4 g, 24.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of terephthalaldehyde (1.34 g, 10.0 mmol, 100 mol%) in THF (100 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 99:1) to furnish the title compound **2a** (2.54 g, 9.0 mmol) in 90% yield as a white solid.

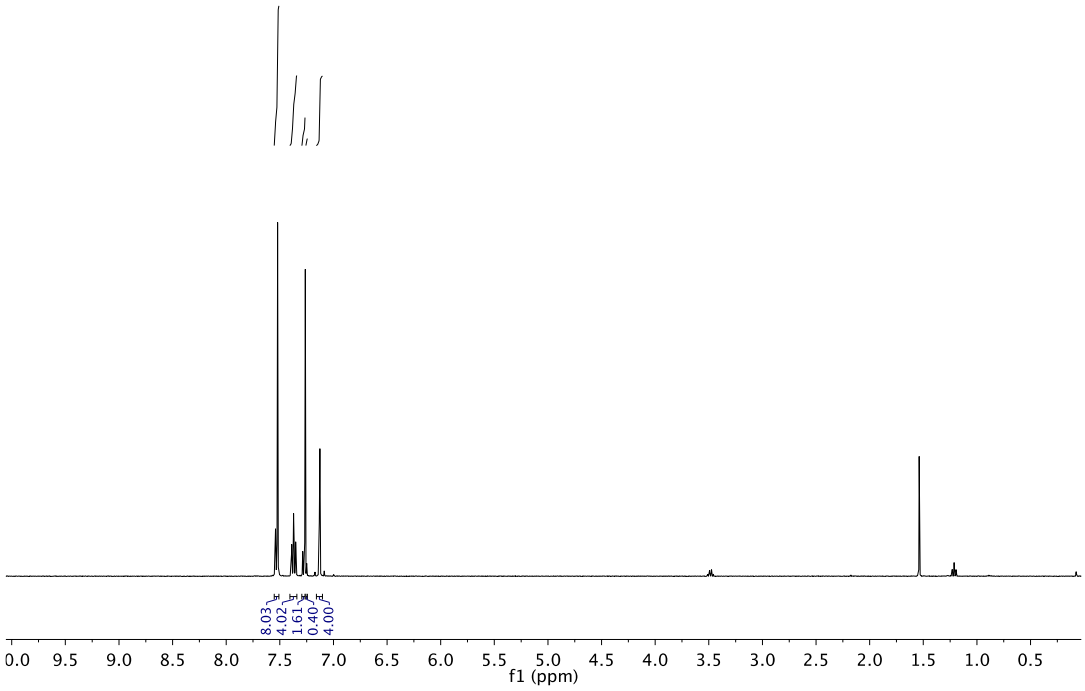
<u>TLC (SiO_2)</u>: R_f = 0.64 (hexanes : ethyl acetate= 90:10).

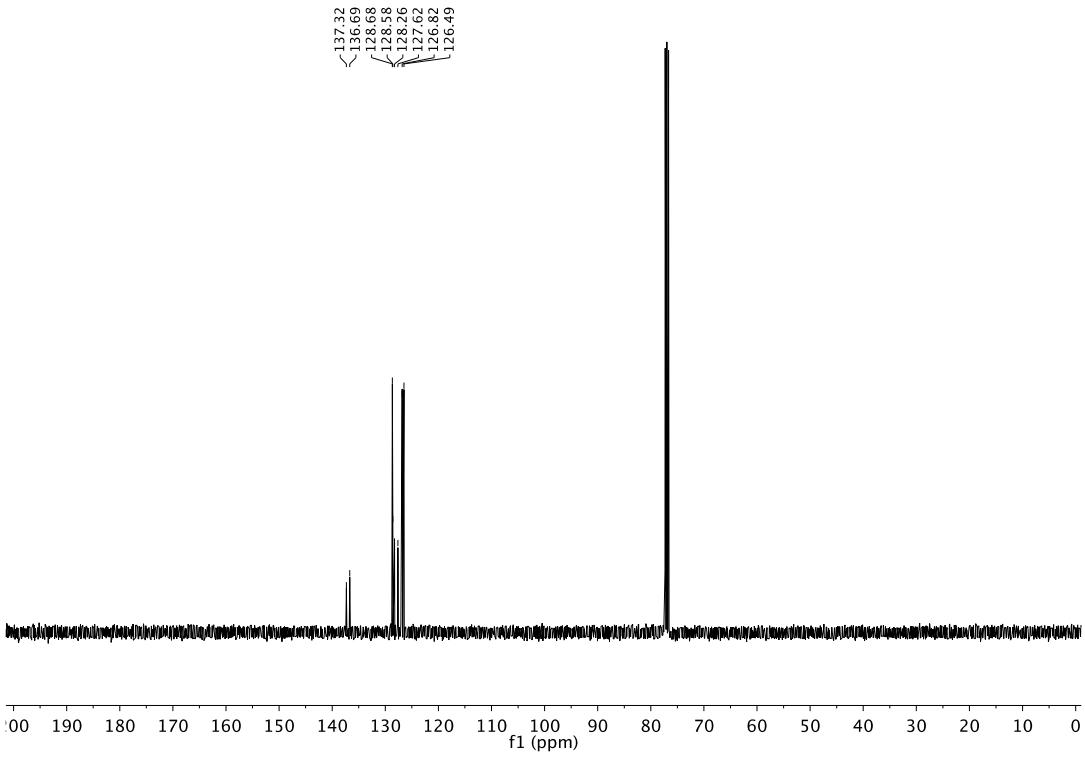
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.55–7.52 (m, 8H), 7.40–7.36 (m, 4H), 7.29–7.24 (m, 2H), 7.13 (t, *J* = 1.4 Hz, 4H) ppm.

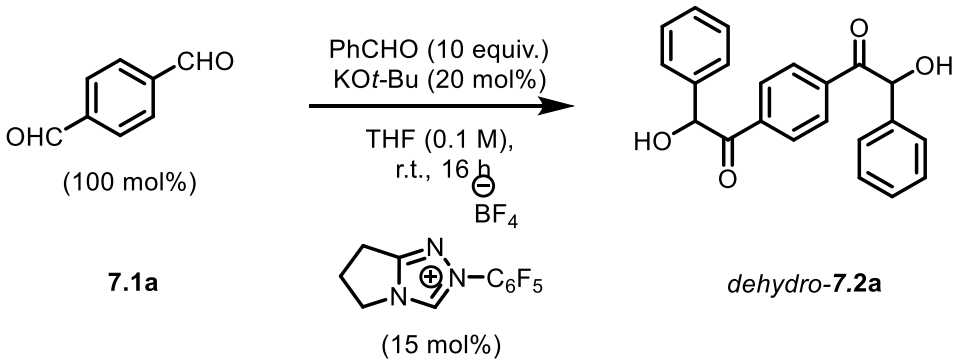
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 137.3, 136.7, 128.7, 128.6, 128.3, 127.6, 126.8, 126.5 ppm.

HRMS: (CI^+) Calculated for $C_{22}H_{18}$ [M^+] = 282.1409, Found 282.1407.

FTIR: (neat): 2357, 969, 816, 691 cm^{-1}.


8.03
4.02
1.61
0.40
4.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


137.32
136.69
128.68
128.58
128.26
127.62
126.82
126.49
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



1,1'-(1,4-phenylene)bis(2-hydroxy-2-phenylethan-1-one) (and other tautomers) (*dehydro*-**7.2a):**

To a solution of terephthalaldehyde (67 mg, 0.5 mmol, 100 mol%), benzaldehyde (0.49 mL, 5.0 mmol, 1000 mol%), and 6,7-dihydro-2-pentafluorophenyl-5H-pyrrolo[2,1,c]-1,2,4-triazolium tetrafluoroborate (27 mg, 0.075 mmol, 15 mol%) in anhydrous THF (5 mL) at ambient temperature was added KOt-Bu (11 mg, 0.1 mmol, 20 mol%). The mixture was allowed to stir for 16 hours. The solution was quenched with water (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried (Na_2SO_4) and volatiles were removed under vacuum. The residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 7:3-1:1) to furnish the title compound *dehydro*-**7.2a** (108 mg, 0.31 mmol) in 62% yield as an off-white solid.

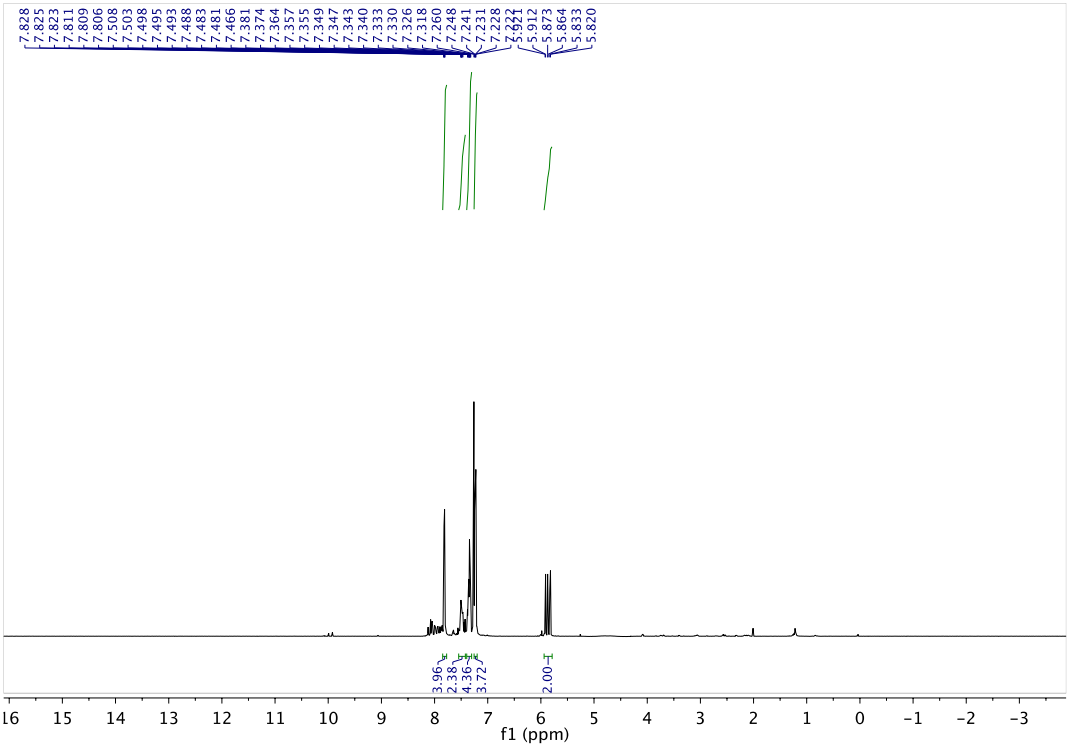
TLC (SiO_2): R_f = 0.14 (hexanes : ethyl acetate = 70:30).

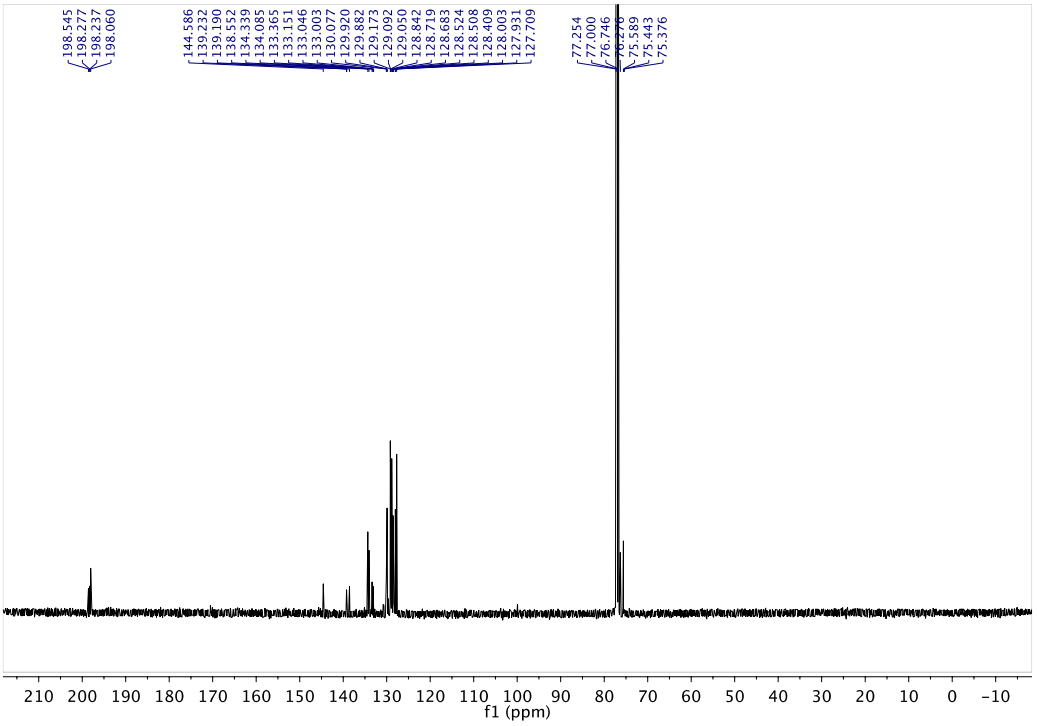
^{1}H NMR: (500 MHz, $CDCl_3$, mixture of isomers): δ = 7.81 (d, *J* = 8Hz, 4H), 7.52-7.42 (m, 2H), 7.40-7.32 (m, 4H), 7.25-7.21 (m, 4H), 5.92 (d, *J* = 4.6 Hz, 2/3 H), 5.87 (d, *J* = 4.8 Hz, 2/3 H), 5.83 (d, *J* = 6.7 Hz, 2/3 H) ppm.

^{13}C NMR: (125 MHz, $CDCl_3$, mixture of isomers): δ = 198.5, 198.3, 198.2, 198.1, 144.6, 139.23, 139.19, 138.6, 134.3, 134.1, 133.4, 133.2, 133.0, 130.1, 129.9, 129.2, 129.1, 128.8, 128.72, 128.68, 128.52, 128.51, 128.4, 128.0, 127.9, 127.7, 76.3, 75.6, 75.44, 75.38 ppm.

HRMS: (ESI^{+}) Calculated for $C_{22}H_{18}O_4$ [M+Na $^{+}$] = 369.1097 , Found 369.1093.

FTIR: (neat): 3390, 2340, 1673, 1256, 1088, 976, 811, 680 cm^{-1}.


7.828
7.825
7.823
7.811
7.809
7.806
7.508
7.503
7.498
7.495
7.493
7.488
7.483
7.481
7.466
7.381
7.374
7.364
7.357
7.355
7.349
7.347
7.343
7.340
7.333
7.330
7.326
7.318
7.260
7.248
7.241
7.231
7.228
5.912
5.873
5.864
5.833
5.820
3.96
2.38
4.36
3.72
2.00
f1 (ppm)


198.545
198.277
198.237
198.060
144.586
139.232
139.190
138.552
134.339
134.085
133.365
133.151
133.046
133.003
130.077
129.920
129.882
129.173
129.092
129.050
128.842
128.719
128.683
128.524
128.508
128.409
128.003
127.931
127.709
77.254
77.000
76.746
75.589
75.443
75.376
f1 (ppm)

Synthesis of bis diol from diene **7.3a**:

To a solution of diene **7.2a** (1.41 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (2.34 g, 10.0 mmol, 200 mol%). The mixture was allowed to stir 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Provided solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 70:30 to 50:50) to furnish the title compound **7.3a** (1.57 g, 3.5 mmol) in 69% yield as a white solid.

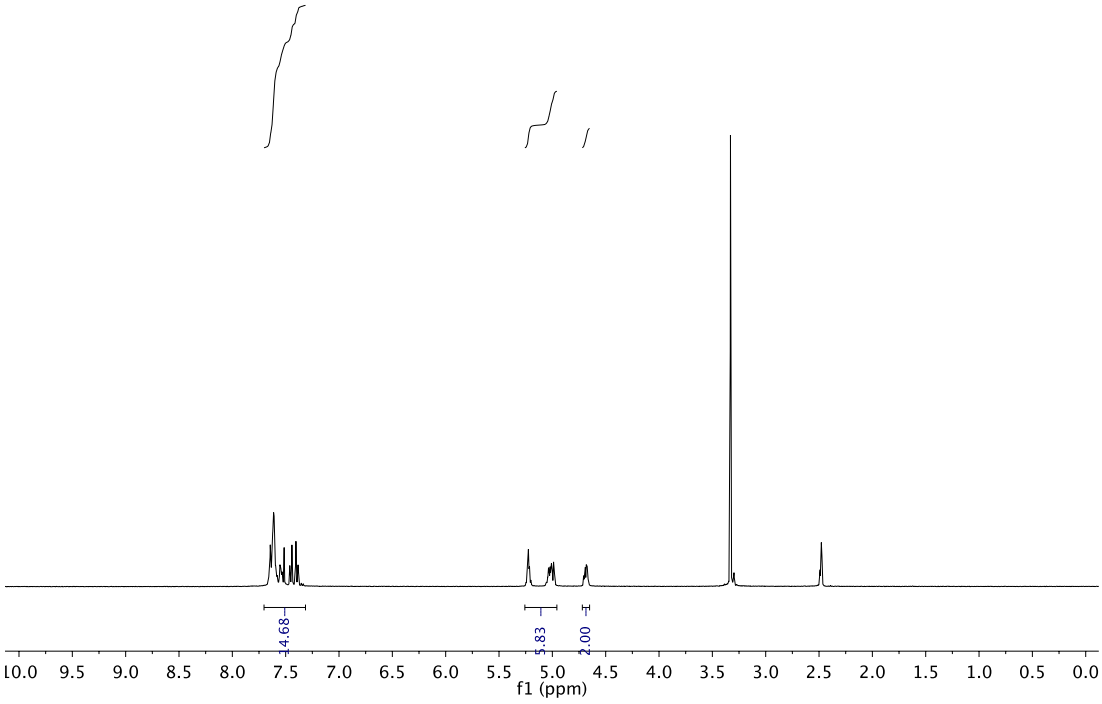
TLC (SiO_2): R_f = 0.58 (ethyl acetate : MeOH = 95:5).

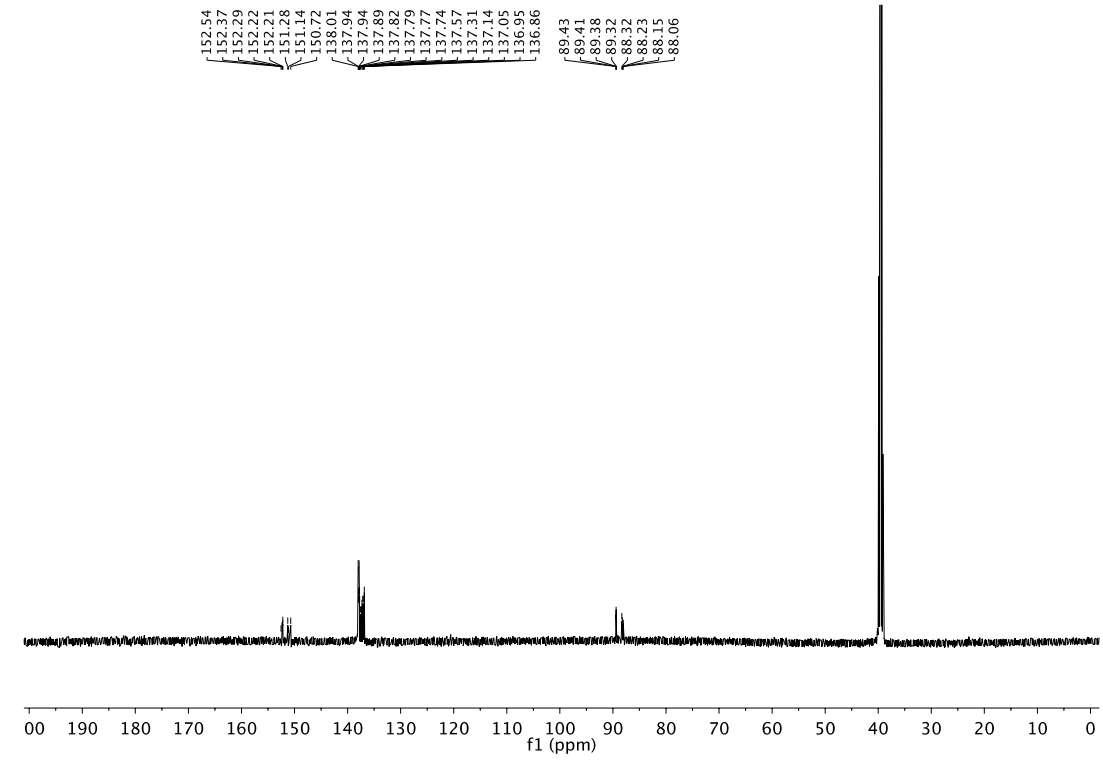
^{1}H NMR: (400 MHz, d_6-DMSO): δ = 7.67–7.38 (m, 14H), 5.24–4.98 (m, 6H), 4.71–4.67 (m, 2H) ppm.

^{13}C NMR: (100 MHz, d_6-DMSO, 3 diastereomers): δ = 152.5, 152.3, 152.3, 152.2, 152.2, 151.3, 151.1, 150.7, 138.0, 137.9, 137.9, 137.8, 137.8, 137.8, 137.7, 137.6, 137.3, 137.1, 137.1, 137.0, 136.9, 89.4, 89.4, 89.4, 89.4, 89.4, 88.3, 88.2, 88.2, 88.1 ppm.

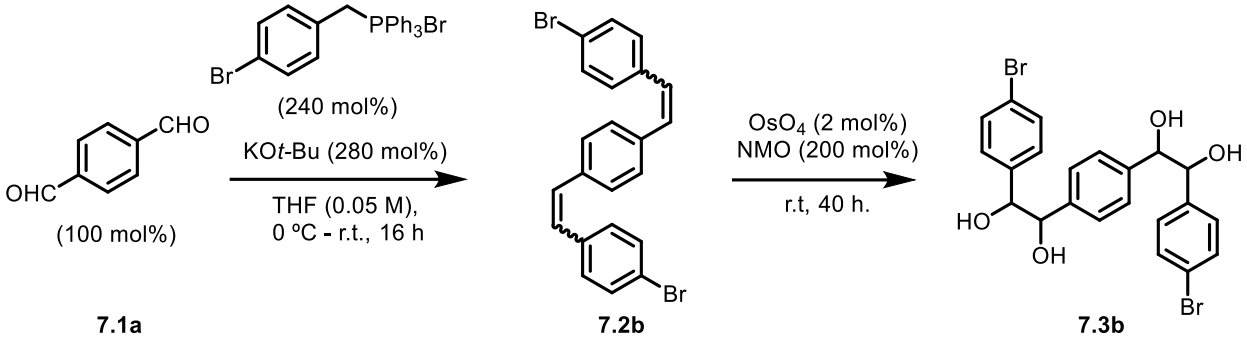
HRMS: (ESI) Calculated for $C_{22}H_{22}O_4$ $[M+Na^+]$ = 373.1410, Found 373.1414.

FTIR: (neat): 2365, 1739, 1366, 1217 cm^{-1}.


4.68
5.83
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.54
152.37
152.29
152.22
152.21
151.28
151.14
150.72
138.01
137.94
137.94
137.89
137.82
137.79
137.77
137.74
137.57
137.31
137.14
137.05
136.95
136.86
89.43
89.41
89.38
89.32
88.32
88.23
88.15
88.06
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2,2'-(1,4-phenylene)bis(1-(4-bromophenyl)ethane-1,2-diol) (7.3b)



Synthesis of diene **7.2b** from terephthalaldehyde:

To a solution of KO*t*-Bu (1.12 g, 28.0 mmol, 280 mol%) in anhydrous THF (100 mL) cooled to 0 ˚C was added Wittig reagent (12.3 g, 24.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of terephthalaldehyde (1.34 g, 10.0 mmol, 100 mol%) in THF (100 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 99:1) to furnish the title compound **7.2b** (3.83 g, 8.7 mmol) in 87% yield as a white solid.

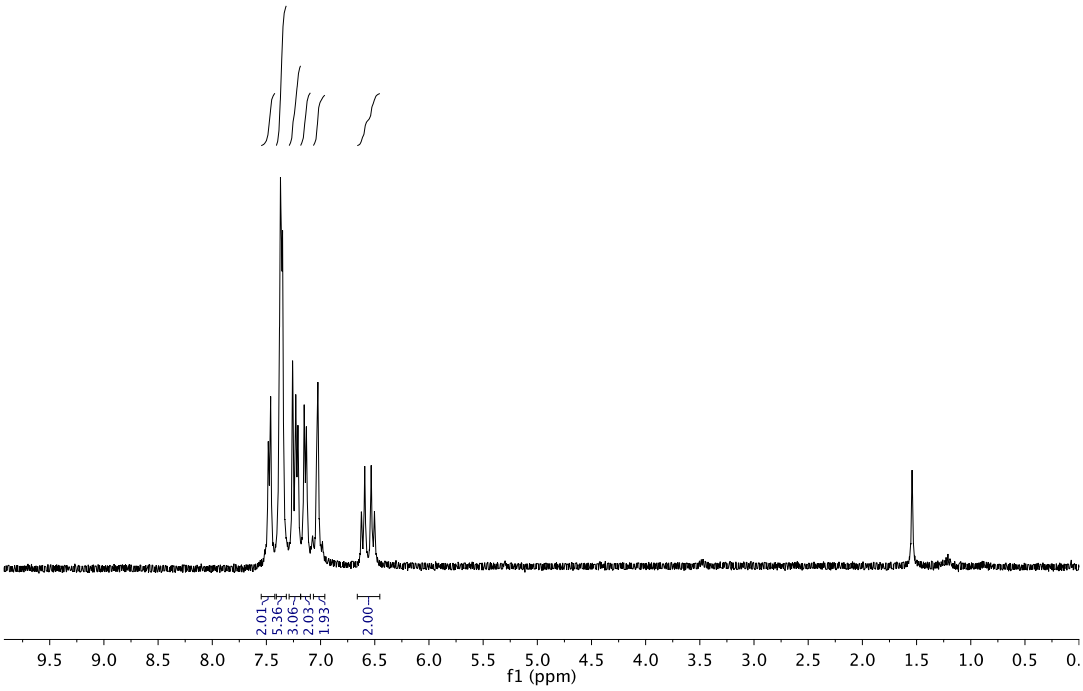
TLC (SiO_2): R_f = 0.78 (hexanes : ethyl acetate = 90:10).

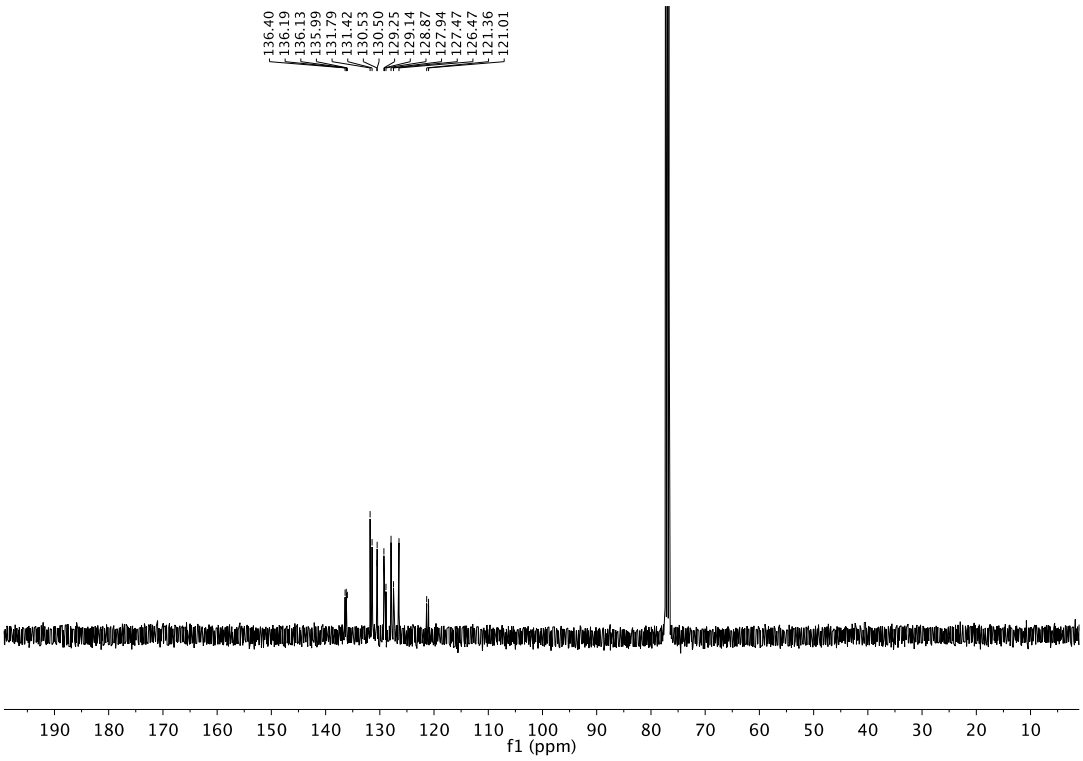
^{1}H NMR: (400 MHz, $CDCl_3$, 2 diastereomers): δ = 7.47 (d, *J* = 8.2 Hz, 2H), 7.38–7.35 (m, 5H), 7.26–7.21 (m, 3H), 7.14(d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 3.0 Hz, 2H), 6.62–6.50 (M, 2H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$, 2 diastereomers): δ = 136.4, 136.2, 136.1, 136.0, 131.8, 131.4, 130.5, 130.5, 129.3, 129.1, 128.9, 127.9, 127.5, 126.5, 121.4, 121.0 ppm.

HRMS: (CI^+) Calculated for $C_{22}H_{16}Br_2$ [M^+] = 439.9598, Found 439.9600.

FTIR: (neat): 2918, 1738, 1366, 1228, 836 cm^{-1}.


2.01
5.36
3.06
2.03
1.93
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


136.40
136.19
136.13
135.99
131.79
131.42
130.53
130.50
129.25
129.14
128.87
127.94
127.47
126.47
121.36
121.01
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Synthesis of bis diol **7.3b** from diene:

To a solution of diene **7.2b** (2.2 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (17 mL) was added NMO in water (w/w 50%) (2.34 g, 10.0 mmol, 200 mol%). The mixture was allowed to stir 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Provided solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 30:70 to 50:50) to furnish the title compound **7.3b** (2.28 g, 4.5 mmol) in 90% yield as a white solid.

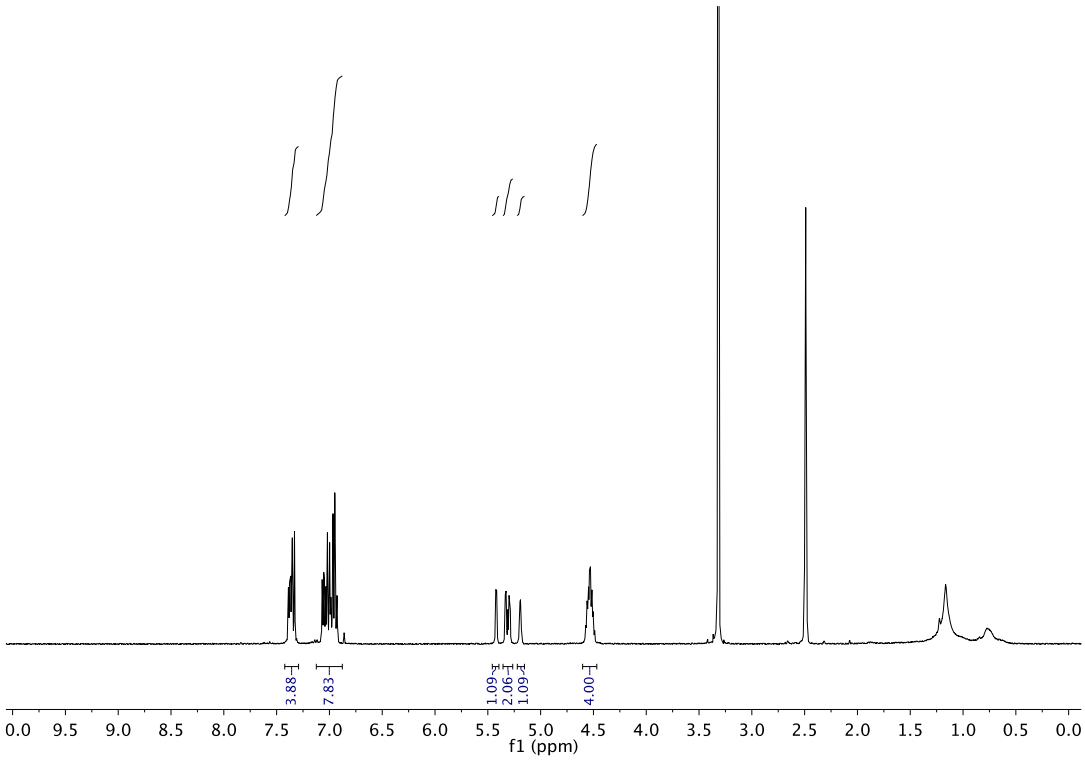
TLC (SiO_2): R_f = 0.58 (ethyl acetate : MeOH = 95:5).

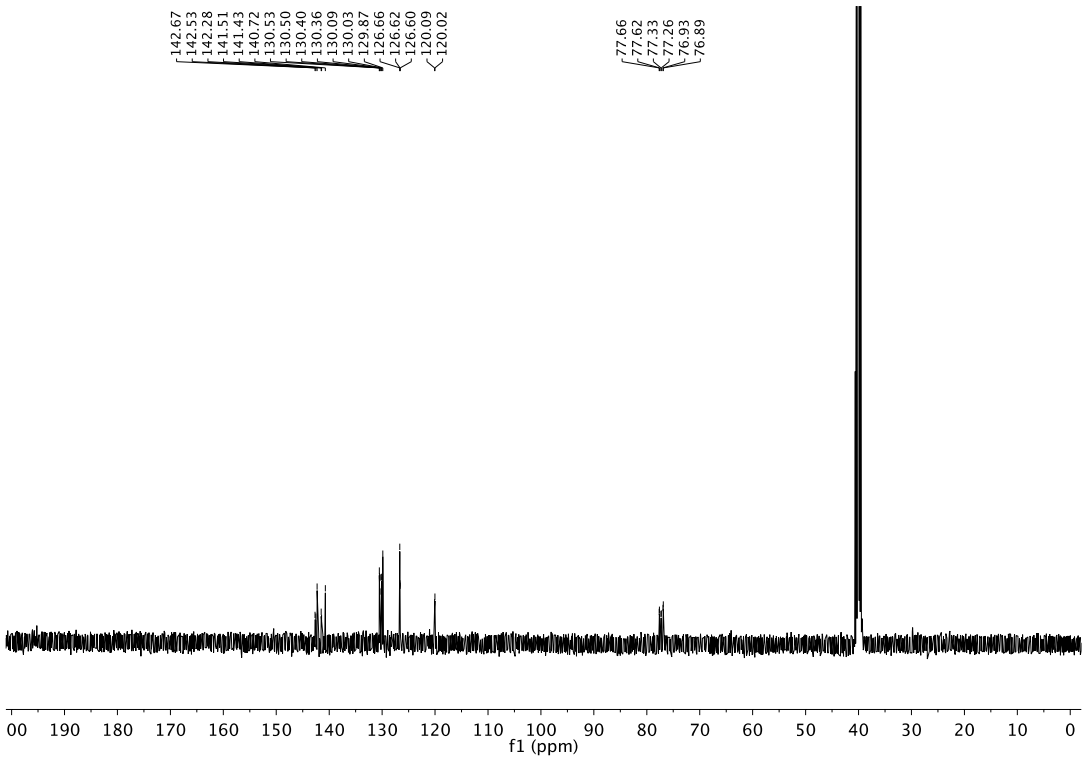
^{1}H NMR: (400 MHz, d_6-DMSO, 3 diastereomers): δ = 7.39–7.33 (m, 4H), 7.07–6.93 (m, 8H), 5.43–5.19 (m, 4H), 4.56–4.50 (m, 4H) ppm.

^{13}C NMR: (100 MHz, d_6-DMSO, 3 diastereomers): δ = 142.7, 142.5, 142.3, 141.5, 141.4, 140.7, 130.5, 130.5, 130.4, 130.4, 130.1, 130.0, 129.9, 126.7, 126.6, 126.6, 120.1, 120.0, 77.7, 77.6, 77.3, 77.3, 76.9, 76.9 ppm.

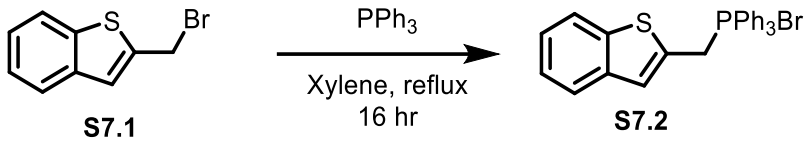
HRMS: (ESI) Calculated for $C_{22}H_{20}Br_2O_4$ [M+Na^+] = 530.9602, Found 530.9609.

FTIR: (neat): 2918, 2849, 1738, 1366, 1217 cm^{-1}.


3.88
7.83
1.09
2.06
1.09
4.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.67
142.53
142.28
141.51
141.43
140.72
130.53
130.50
130.40
130.36
130.09
130.03
129.87
126.66
126.62
126.60
120.09
120.02
77.66
77.62
77.33
77.26
76.93
76.89
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

(benzo[*b*]thiophen-2-ylmethyl)bromotriphenylphosphane (S7.2)



S7.1 **S7.2**

Bromide **S7.1** was synthesized according to known procedures[29] and their characterization data[30] match our own in all respects.

To 2-Bromomethylbenzothiophene (3.31 g, 15.0 mmol, 100 mol%) in xylene (30 mL) was added triphenylphosphine (3.93 g, 15.0 mmol, 100 mol%). The mixture was stirred under reflux for 16 h. Then, the reaction mixture was allowed to cool down to room temperature. The precipitation was filtrated, and the residue was washed with toluene and hexanes to furnish the title compound **S7.2** (6.90 g, 14.1 mmol) in 94% yield as a white solid.

TLC (SiO_2): R_f = 0.20 (MeOH = 100).

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.85–7.76 (m, 9H), 7.65–7.58 (m, 9H), 7.29–7.23 (m, 2H), 5.96 (d, *J* = 14.1 Hz, 2H) ppm.

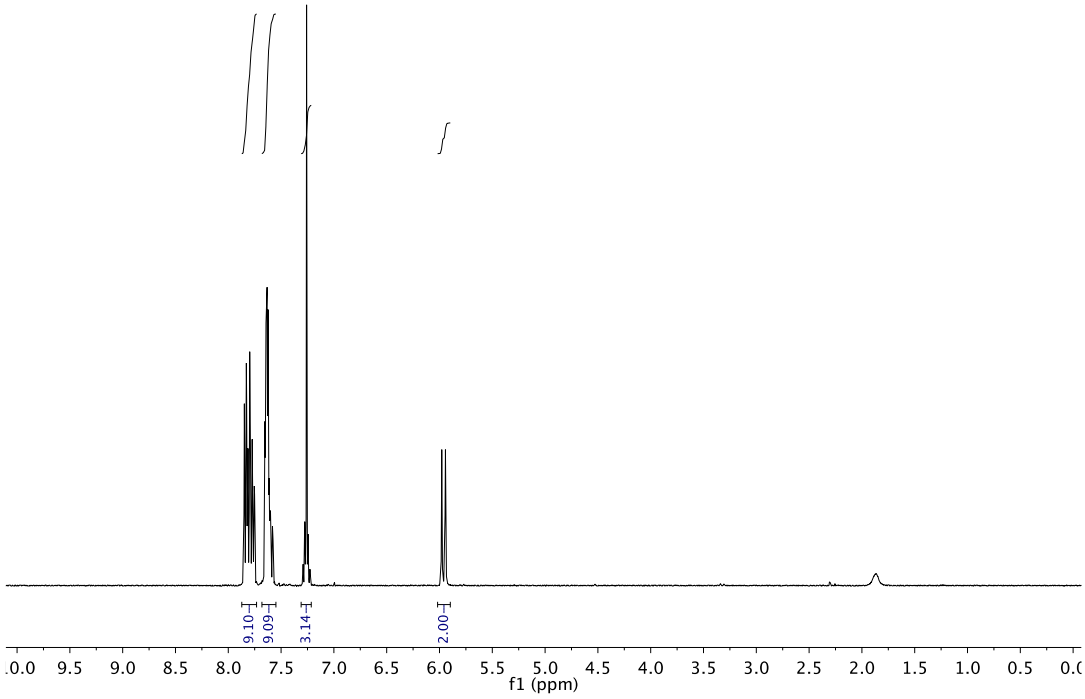
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 139.9, 135.1, 135.0, 134.3, 134.2, 130.2, 130.0, 124.7, 124.5, 123.9, 121.8, 118.0, 117.2 ppm.

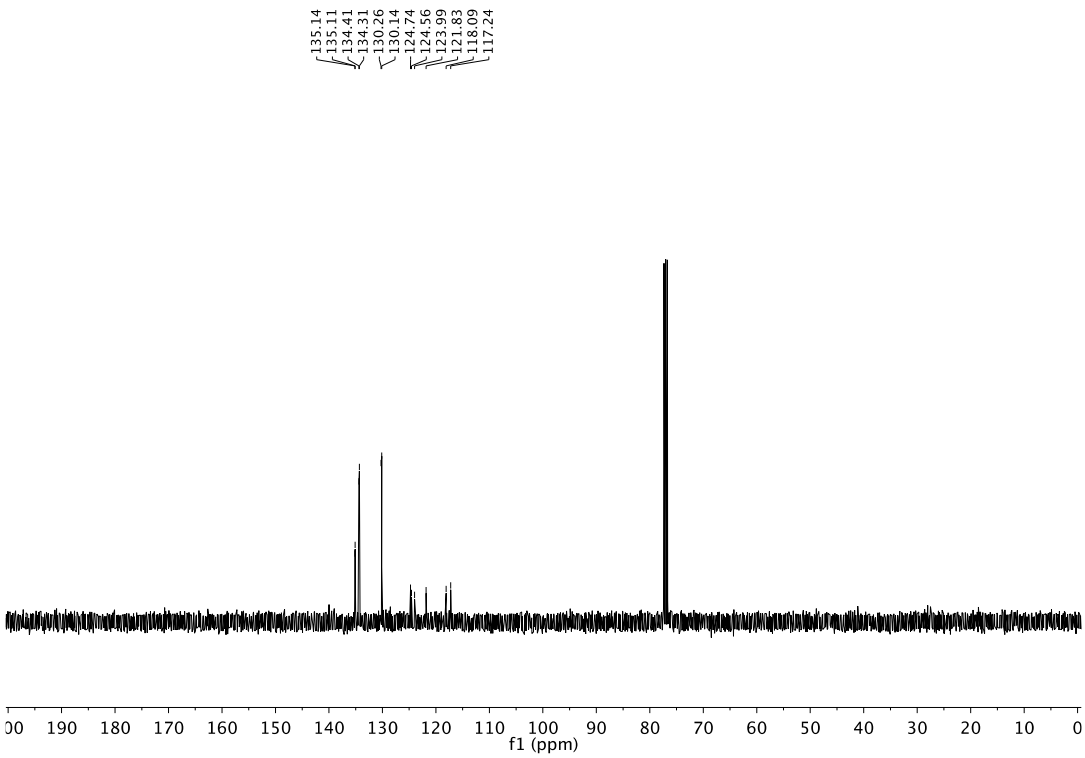
^{31}P NMR: (160 MHz, $CDCl_3$): *δ* 21.3 ppm (85% H_3PO_4 was used as internal standard 0 ppm).

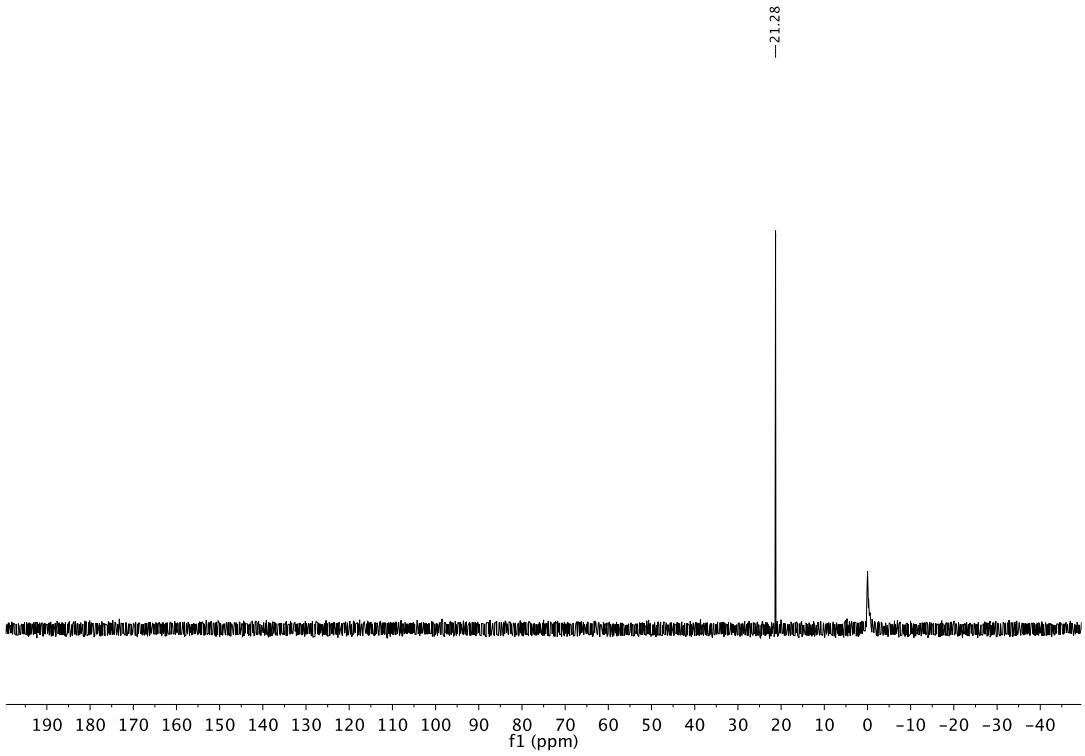
HRMS: (ESI) Calculated for $C_{27}H_{22}PS$ [M^+] =409.11740, Found 409.11860.

FTIR: (neat): 3032, 3010, 2835, 2774, 1738, 1438, 1225, 1109, 710, 686 cm^{-1}.

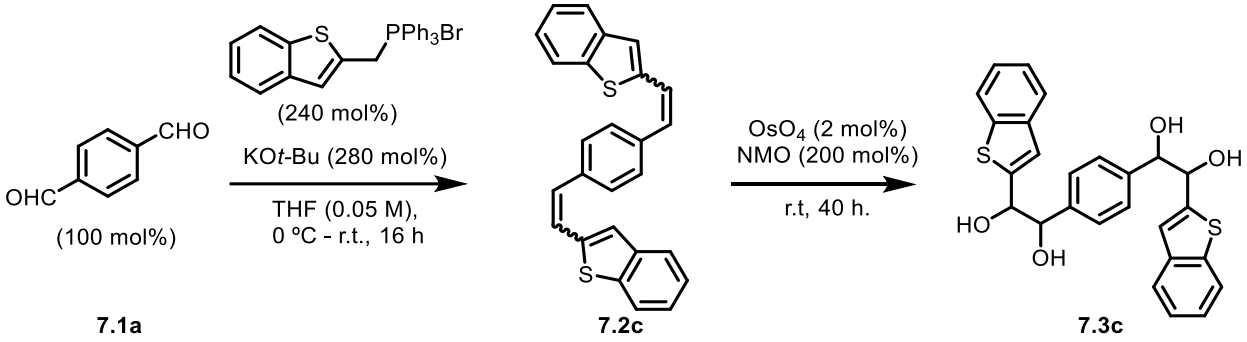
Melting Point : 262-263 °C


9.10
9.09
3.14
2.00
f1 (ppm)


135.14
135.11
134.41
134.31
130.26
130.14
124.74
124.56
123.99
121.83
118.09
117.24
f1 (ppm)


21.28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

2,2'-(1,4-phenylene)bis(1-(benzo[*b*]thiophen-2-yl)ethane-1,2-diol) (7.3c)



7.1a **7.2c** **7.3c**

Synthesis of diene **7.2c** from terephthalaldehyde:

To a solution of KO*t*-Bu (1.12 g, 28.0 mmol, 280 mol%) in anhydrous THF (100 mL) cooled to 0 ˚C was added Wittig reagent (11.7 g, 24.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of terephthalaldehyde (1.34 g, 10.0 mmol, 100 mol%) in THF (100 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:DCM = 90:10) to furnish the title compound **7.2c** (2.84 g, 7.2 mmol, *Z*,*Z*:*E*,*Z* = 1:1) in 72% yield as a yellow solid.

TLC (SiO_2): R_f = 0.78 (DCM:hexanes= 1:8).

^{1}H NMR: (400 MHz, $CDCl_3$, *Z*,*Z* isomer): δ 7.59–7.56 (m, 4H), 7.35 (s, 4H), 7.28–7.22 (m, 4H), 7.25 (s, 2H), 6.74 (d, *J* = 12.0 Hz, 2H), 6.66 (d, *J* = 12.0 Hz, 2H) ppm.

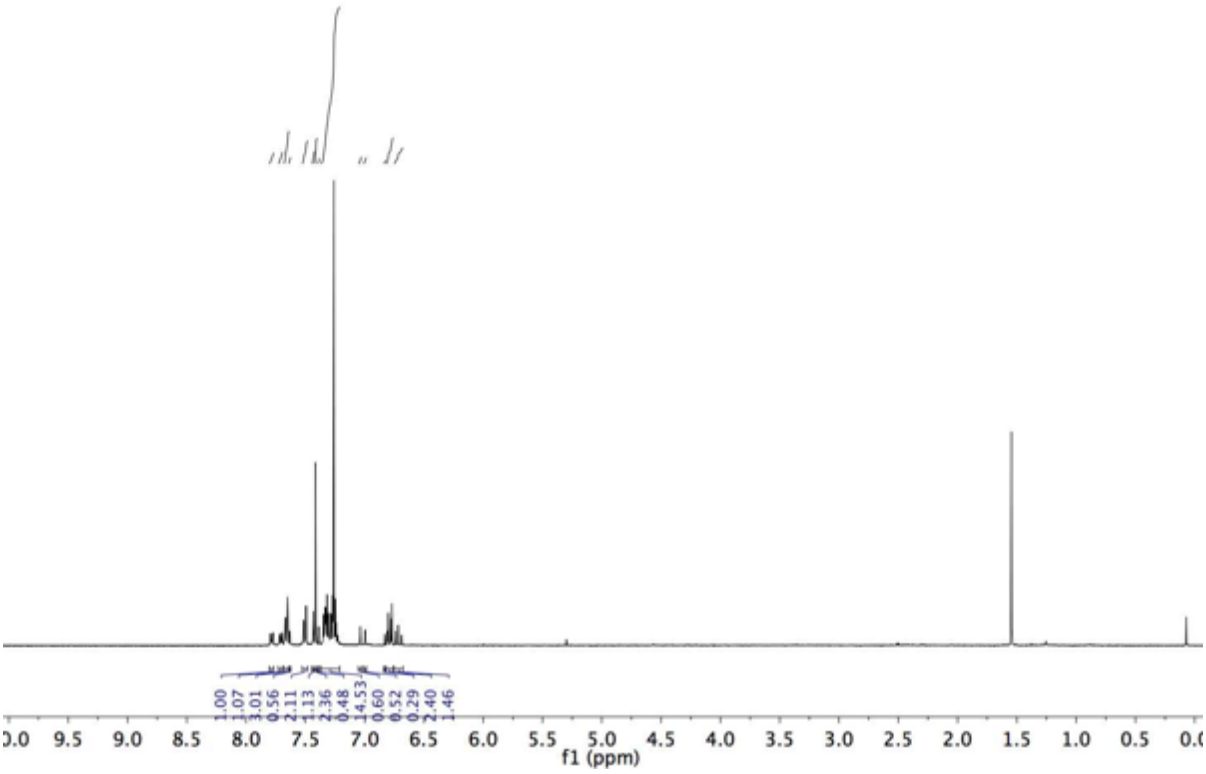
^{1}H NMR: (400 MHz, $CDCl_3$, *E*,*Z* isomer): δ 7.79–7.77 (m, 1H), 7.72–7.70 (m, 1H), 7.67–7.64 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 16.0 Hz, 2H), 7.37 (d, *J* = 16.0 Hz, 1H), 7.33–7.30 (m, 2H), 7.29–7.26 (m, 2H), 7.26 (s, 1H), 7.25 (s, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.79 (d, *J* = 11.7 Hz, 1H), 6.70 (d, *J* = 11.7 Hz, 1H) ppm.

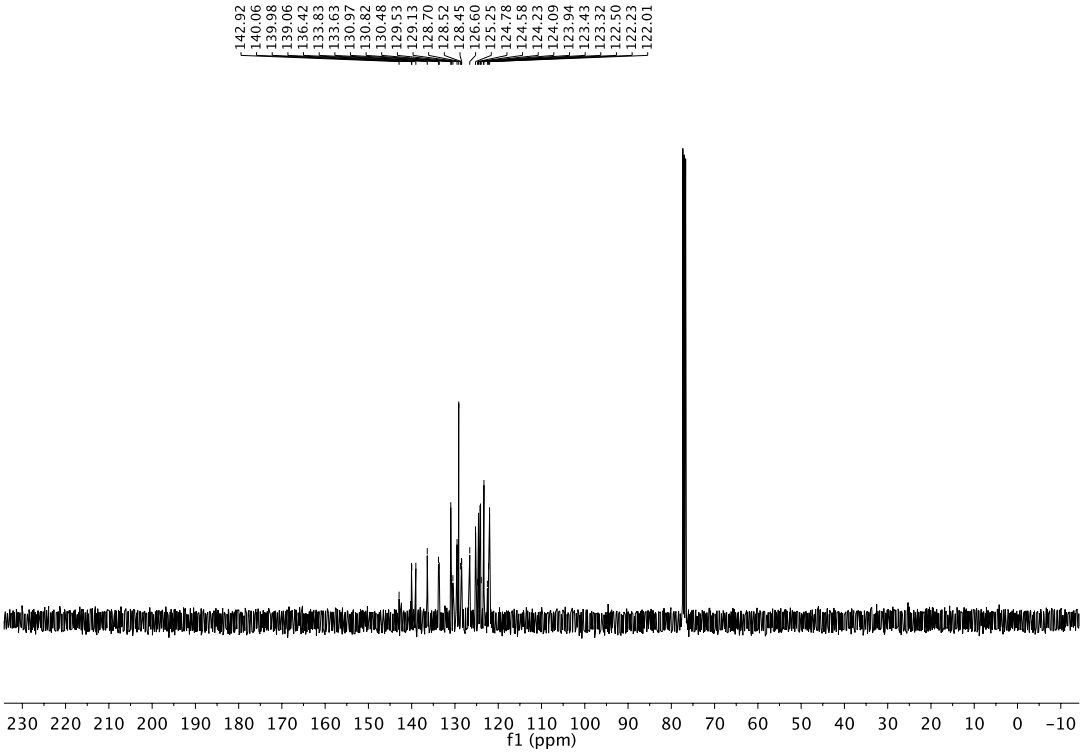
^{13}C NMR: (100 MHz, $CDCl_3$, *Z*,*Z* isomer and *E*,*Z* isomer): δ 142.9, 140.2, 140.0, 140.0, 139.9, 139.1, 139.0, 138.9, 136.5, 136.4, 136.1, 133.8, 133.6, 130.9, 130.8, 130.5, 129.5, 129.1, 129.1, 128.7, 128.5, 128.4, 126.6, 125.2, 125.2, 124.8, 124.6, 124.6, 124.5, 124.2, 124.2, 124.1, 123.9, 123.4, 123.3, 122.5, 122.2, 122.0, 122.0 ppm.

HRMS: (CI^+) Calculated for $C_{26}H_{18}S_2$ [M^+] =394.0850, Found 394.0852.

FTIR: (neat) 3053, 3017, 2945, 1625, 1587, 1455, 1147, 1014, 962, 743 cm^{-1}.

Melting Point : >360 °C (color change : yellow to black)


1.00
1.07
3.01
0.56
2.11
1.13
2.36
0.48
14.53
0.60
0.52
0.29
2.40
1.46
f1 (ppm)


142.92
140.06
139.98
139.06
136.42
133.83
133.63
130.97
130.82
130.48
129.53
129.13
128.70
128.52
128.45
126.60
125.25
124.78
124.58
124.23
124.09
123.94
123.43
123.32
122.50
122.23
122.01
f1 (ppm)

Synthesis of bis diol **7.3c** from diene **7.2c**:

To a solution of diene **7.2c** (1.47 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (2.34 g, 10.0 mmol, 200 mol%). The mixture was allowed to stir 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Provided solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 1:1) to furnish the title compound **7.3c** (1.55 g, 3.4 mmol) in 67% yield as a white solid.

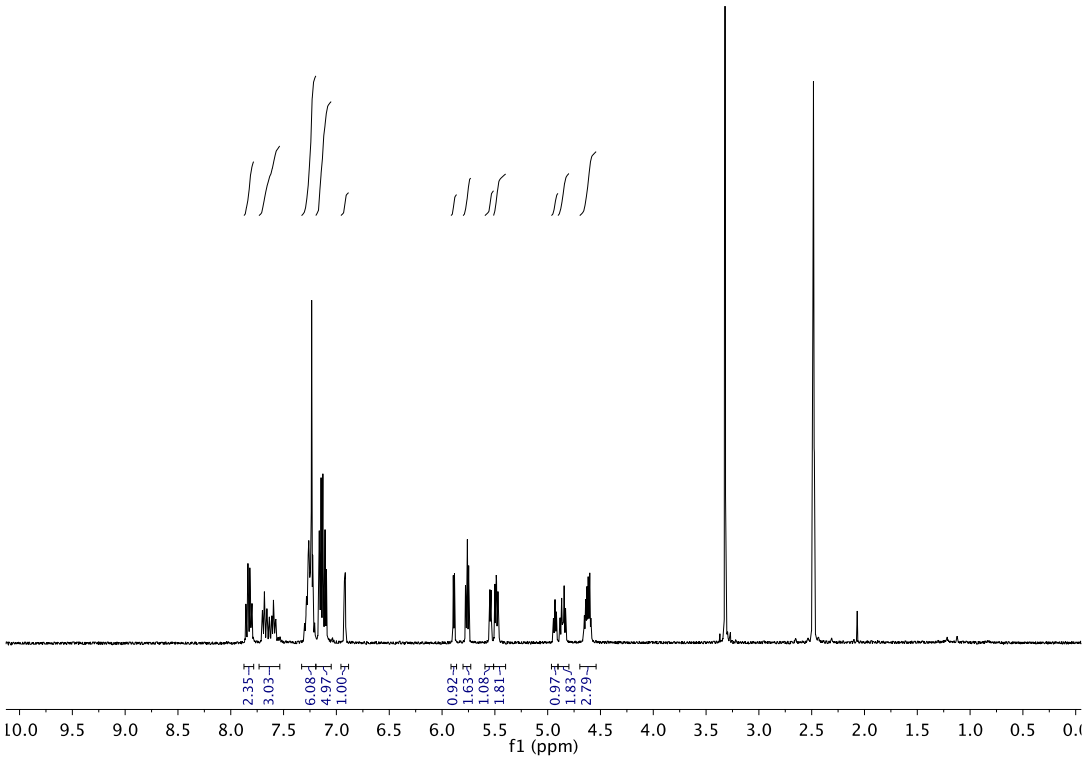
TLC (SiO_2): R_f = 0.25 (hexanes : ethyl acetate = 1:2).

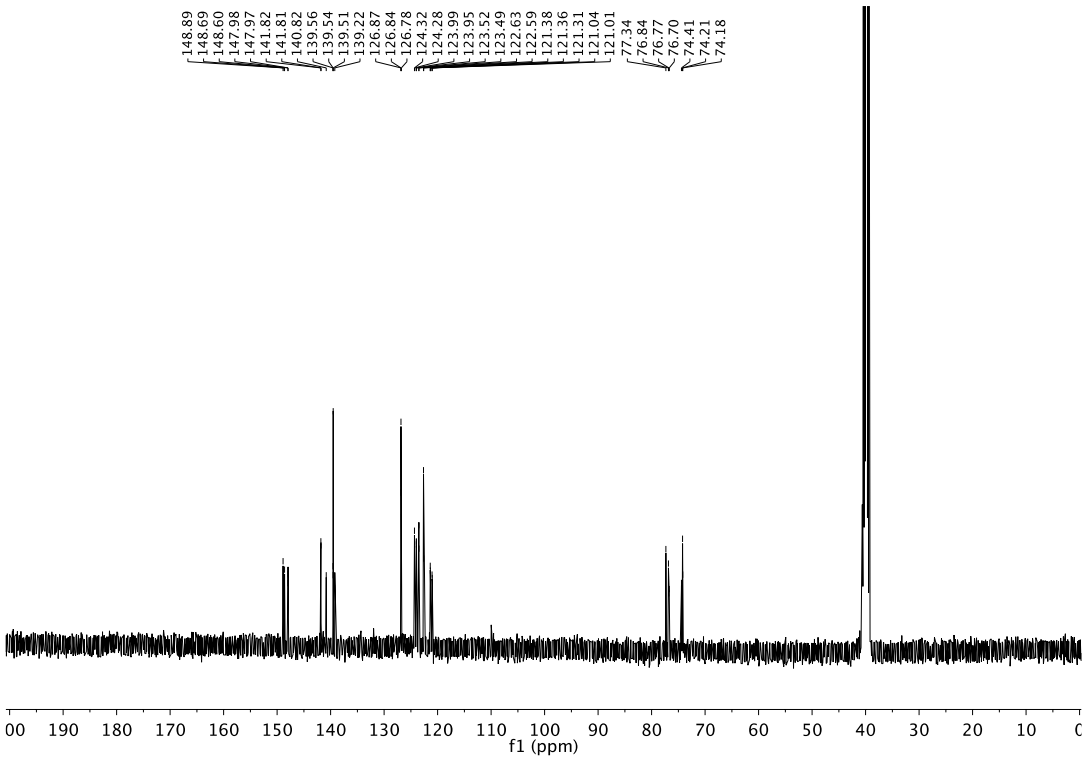
^{1}H NMR: (400 MHz, DMSO-d6, isomer mixture): δ 7.87–7.82 (m, 2H), 7.72–7.59 (m, 2H), 7.30–6.93 (m, 10H), 5.91–4.61 (m, 2H) ppm.

^{13}C NMR: (100 MHz, DMSO-d6, isomer mixture): δ 148.5, 148.2, 148.2, 147.5, 147.5, 141.4, 140.4, 139.1, 138.8, 126.4, 126.3, 123.9, 123.8, 123.5, 123.1, 122.2, 121.0, 120.9, 120.9, 120.6, 120.6, 76.9, 76.4, 76.3, 76.2, 74.0, 73.8 ppm

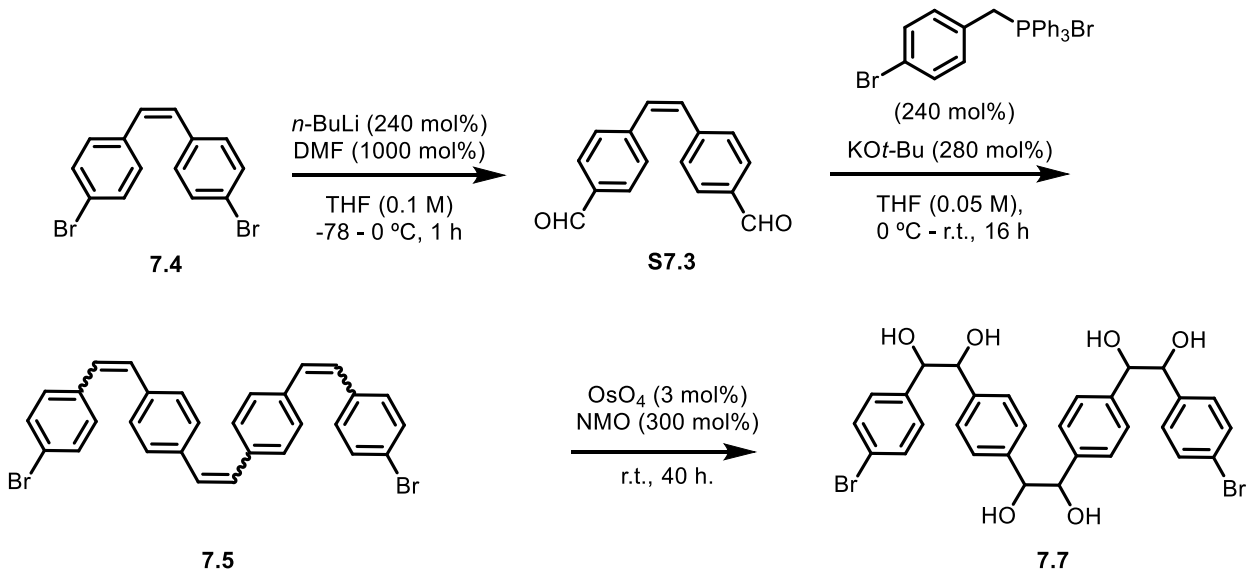
HRMS: (ESI) Calculated for $C_{26}H_{22}O_4S_2$ [M+Na^+] = 485.08520, Found 485.08570.

FTIR: (neat) 3349, 3057, 2890, 1688, 1456, 1036, 1013, 837, 741, 694 cm^{-1}.


2.35
3.03
6.08
4.97
1.00
0.92
1.63
1.08
1.81
0.97
1.83
2.79
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


148.89
148.69
148.60
147.98
147.97
141.82
141.81
140.82
139.56
139.54
139.51
139.22
126.87
126.84
126.78
124.32
124.28
123.99
123.95
123.52
123.49
122.63
122.59
121.38
121.36
121.31
121.04
121.01
77.34
76.84
76.77
76.70
74.41
74.21
74.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2,2'-((1,2-dihydroxyethane-1,2-diyl)bis(4,1-phenylene))bis(1-(4-bromophenyl)ethane-1,2-diol) (7.7)



Bromide **7.4** was synthesized according to known procedures[31] and their characterization data match our own in all respects.

Synthesis of dialdehyde **S7.3** from diene **7.4**:

To a solution of alkene **7.4** (5.07 g, 15 mmol, 100 mol%) in anhydrous THF (150 mL) cooled to -78 ˚C was added *n*-BuLi (2.5 M in hexanes, 14.4 mL, 36.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of freshly distilled DMF (11.6 mL, 150 mmol, 1000 mol%). The reaction was then warmed to 0 ˚C and allowed to stir for 1 hour. The reaction was subsequently quenched by the addition of saturated NH_4Cl solution (50 mL). The aqueous layer was then extracted with Et_2O (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided a solid which was subjected to flash column chromatography (SiO_2;

hexanes: ethyl acetate = 4:1) to furnish the title compound **S7.3** (2.66 g, 11.3 mmol) in 75% yield as a white solid.

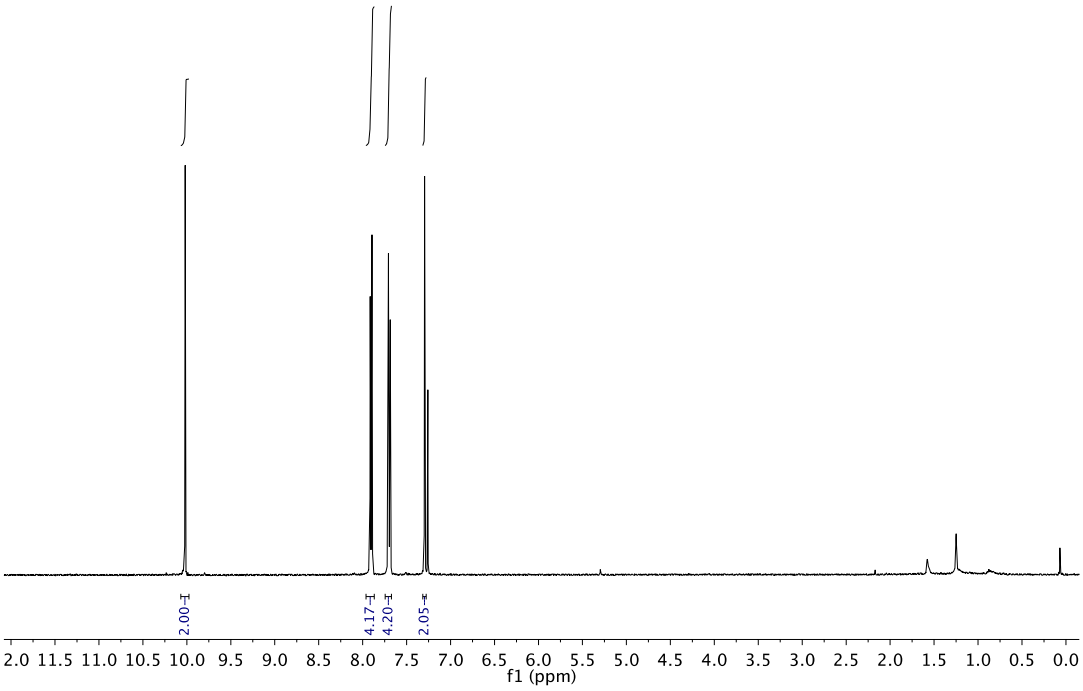
TLC (SiO_2): R_f = 0.28 (hexanes : ethyl acetate = 70:30).

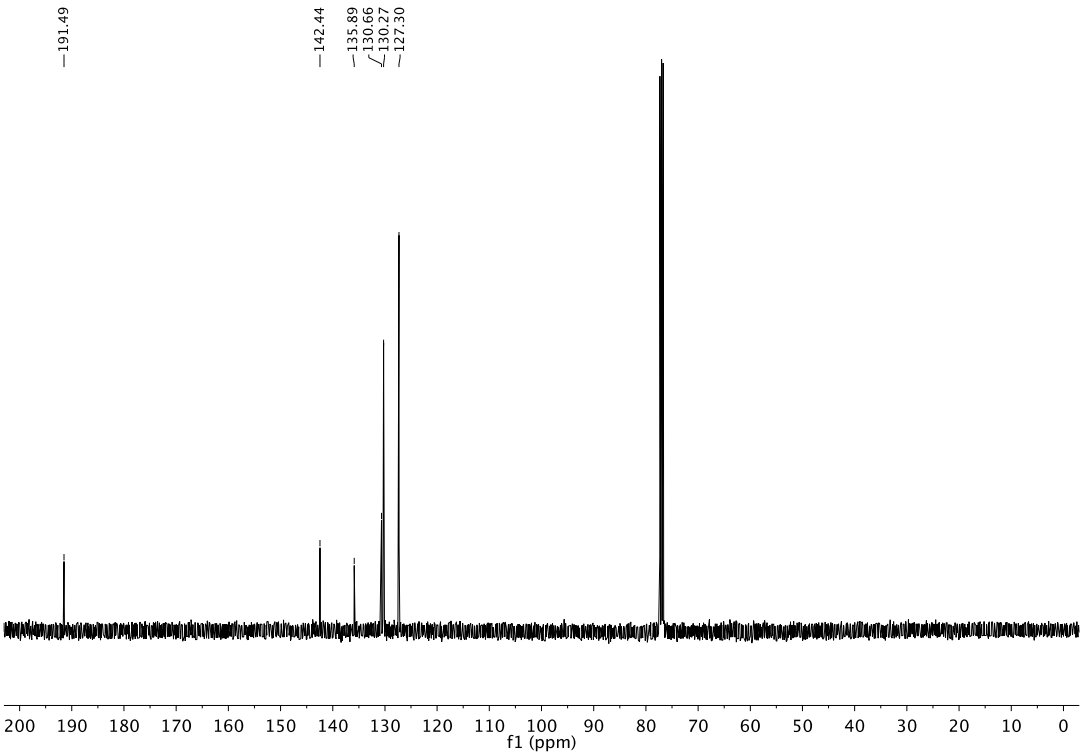
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 10.0 (s, 2H), 7.90 (d, *J* = 7.9 Hz, 4H), 7.69 (d, *J* = 7.9 Hz, 4H), 7.30 (s, 2H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$): δ = 191.5, 142.4, 135.9, 130.7, 130.3, 127.3 ppm.

HRMS: (Cl+) Calculated for $C_{16}H_{12}O_2$ [M^+] = 236.0837, Found 236.0840.

FTIR: (neat): 2918, 2849, 1737, 1366, 1217 cm^{-1}.


2.00
4.17
4.20
2.05
f1 (ppm)


191.49
142.44
135.89
130.66
130.27
127.30
f1 (ppm)

Synthesis of triene **7.5** from dialdehyde **S7.3**:

To a solution of KO*t*-Bu (1.12 g, 28.0 mmol, 280 mol%) in anhydrous THF (100 mL) cooled to 0 ˚C was added phosphonium salt (12.3 g, 24.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of dicarbonyl **S7.3** (2.36 g, 10.0 mmol, 100 mol%) in THF (100 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 97.5:2.5) to furnish the title compound **7.5** (3.69 g, 6.8 mmol) in 68% yield as a yellow solid.

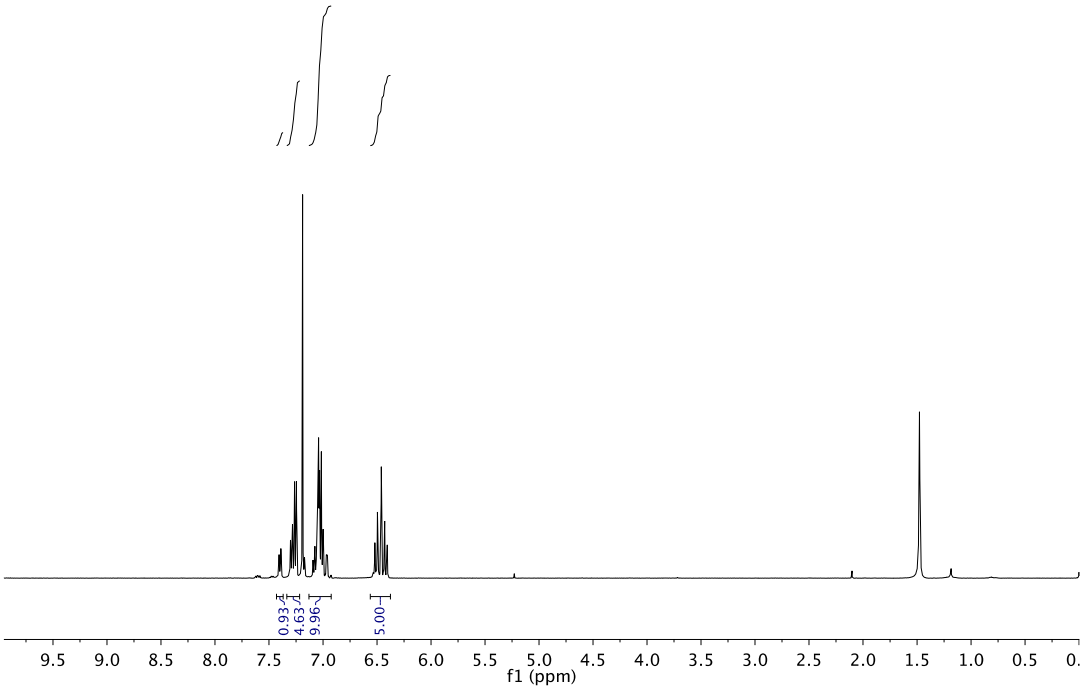
TLC (SiO_2): R_f = 0.73 (hexanes : ethyl acetate = 90:10).

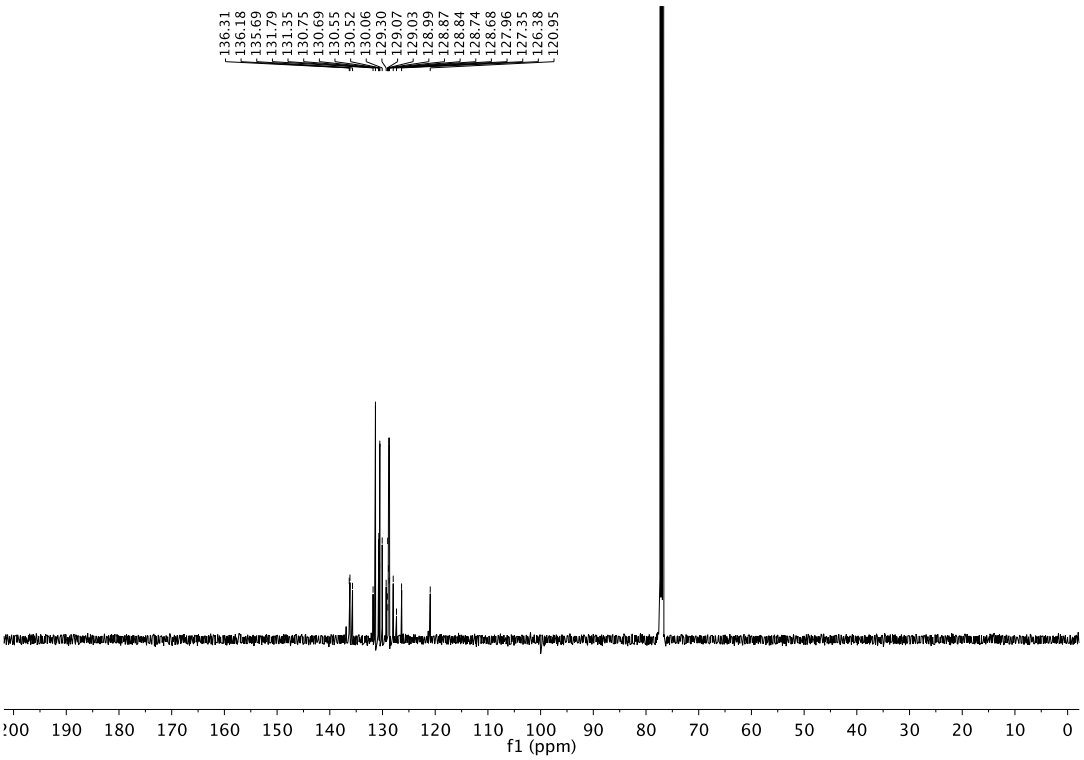
^{1}H NMR: (400 MHz, $CDCl_3$, 3 diastereomers): δ = 7.41–7.39 (m, 1H), 7.30–7.24 (m, 5H), 7.09–6.96 (m, 10H), 6.52–6.40 (m, 5H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$, 3 diastereomers): δ = 136.3, 136.2, 135.7, 131.8, 131.4, 130.8, 130.7, 130.6, 130.5, 130.0, 129.3, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.7, 128.0, 127.4, 126.4, 121.0 ppm.

HRMS: (CI) Calculated for $C_{30}H_{22}Br_2$ [M^+] = 542.0068, Found 542.0058.

FTIR: (neat): 1738, 1366, 1216 cm^{-1}.


0.93
4.63
9.96
5.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


136.31
136.18
135.69
131.79
131.35
130.75
130.69
130.55
130.52
130.06
129.30
129.07
129.03
128.99
128.87
128.84
128.74
128.68
127.96
127.35
126.38
120.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Synthesis of tris diol **7.7** from triene **7.5**:

To a solution of triene **7.5** (2.71 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (3.51 g, 15.0 mmol, 300 mol%). The mixture was allowed to stir 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Provided solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 1:1 to ethyl acetate = 1) to furnish the title compound **7.7** (2.26 g, 3.5 mmol) in 70% yield as a white solid.

TLC (SiO_2): R_f = 0.42 (ethyl acetate : MeOH = 95:5).

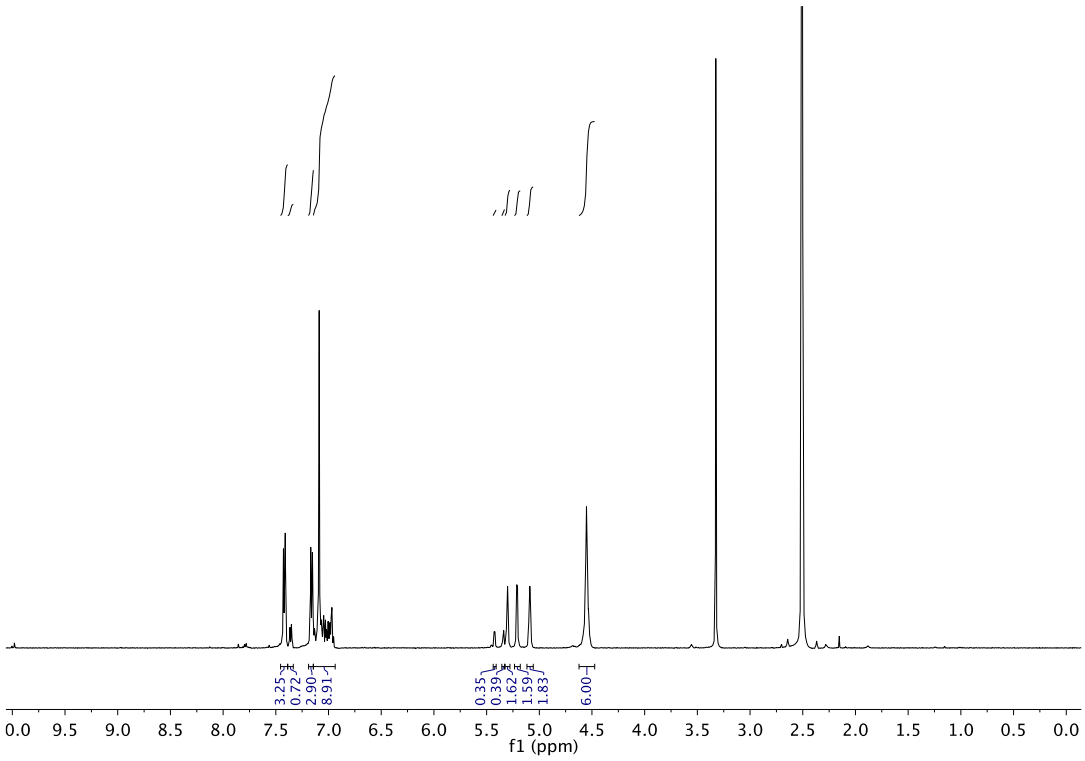
^{1}H NMR: (400 MHz, d_6-DMSO): major diastereomer δ = 7.45–7.40 (m, 4H), 7.18–7.13 (m, 4H), 7.07–6.95 (m, 8H), 5.31 (d, *J* = 3.9 Hz, 2H), 5.21 (d, *J* = 3.9 Hz, 2H), 5.11–5.07 (m, 2H), 4.62–4.51 (m, 6H) ppm.

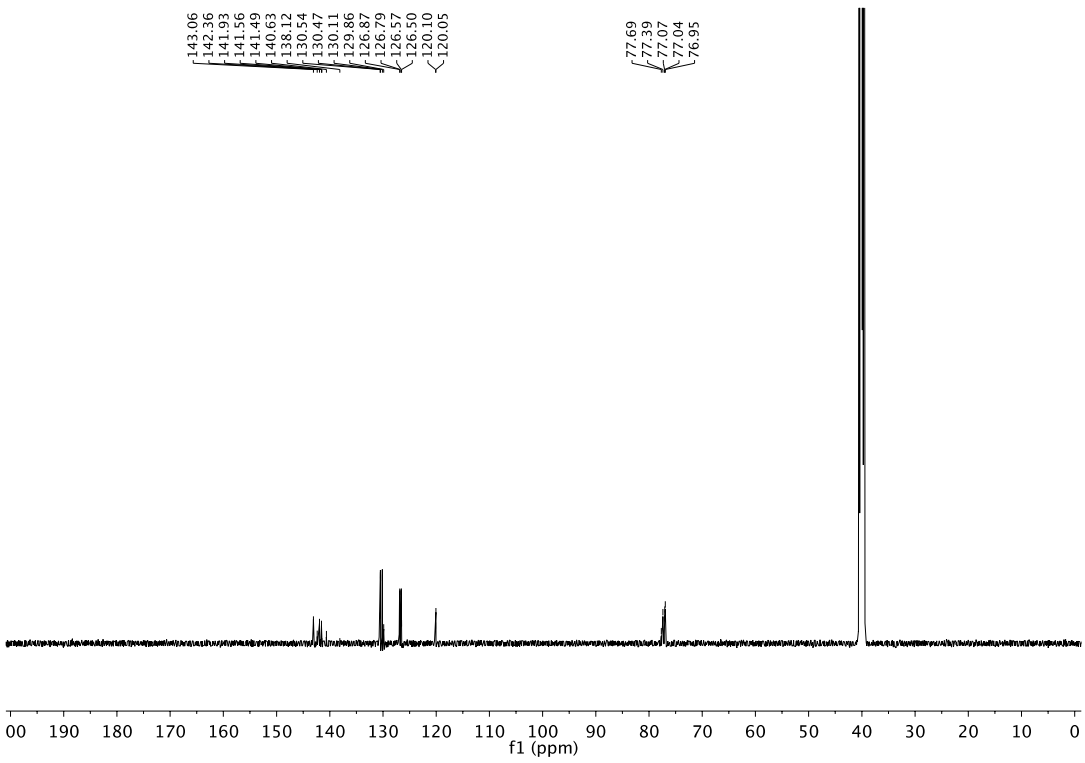
^{1}H NMR: (400 MHz, d_6-DMSO): minor diastereomer δ = 7.37–7.35 (m, 4H), 7.07–6.95 (m, 12H), 5.42 (d, *J* = 4.3 Hz, 2H), 5.34 (d, *J* = 4.3 Hz, 2H), 5.11–5.07 (m, 2H), 4.62– 4.51 (m, 6H) ppm.

^{13}C NMR: (100 MHz, d_6-DMSO, 2 diastereomers): δ = 143.1, 142.4, 141.9, 141.6, 141.5, 140.6, 138.1, 130.5, 130.5, 130.1, 129.9, 126.9, 126.8, 126.6, 126.5, 120.1, 120.1, 77.7, 77.4, 77.1, 77.0, 77.0 ppm.

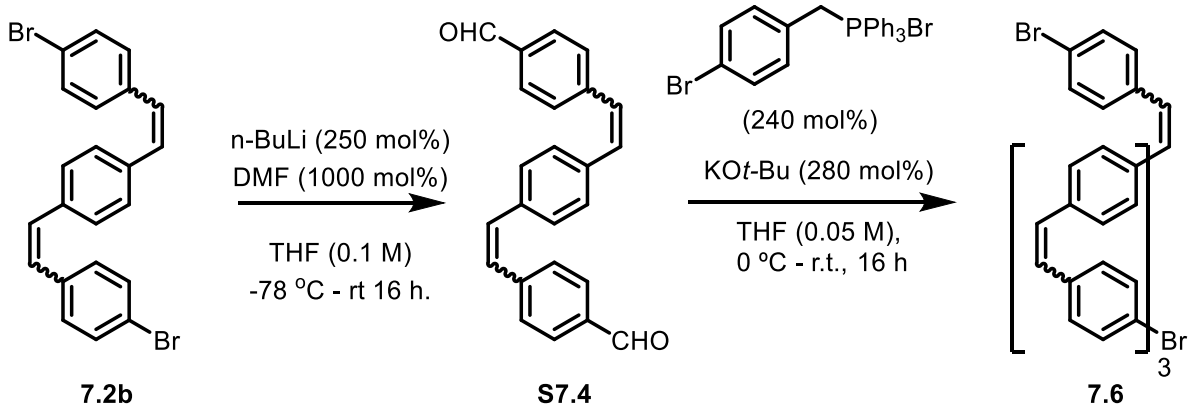
HRMS: (ESI) Calculated for $C_{30}H_{28}Br_2O_6$ [M+H$^+$] = 667.0127, Found 667.0124.

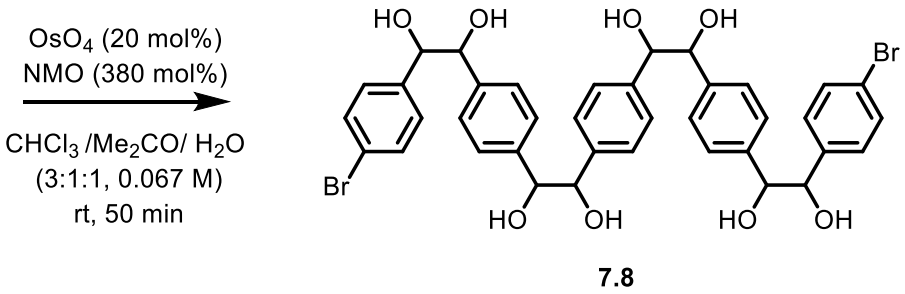
FTIR: (neat): 3365, 2359, 1030 cm^{-1}.


3.25
0.72
2.90
8.91
0.35
0.39
1.62
1.59
1.83
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.06
142.36
141.93
141.56
141.49
140.63
138.12
130.54
130.47
130.11
129.86
126.87
126.79
126.57
126.50
120.10
120.05
77.69
77.39
77.07
77.04
76.95
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2,2'-(1,4-phenylene)bis(1-(4-(2-(4-bromophenyl)-1,2-dihydroxyethyl)phenyl)ethane-1,2-diol) (7.8)





7.8

Dialdehyde **S4** was synthesized analogously to known procedures[33] and their characterization data is identical in all respects.

Synthesis of 1,4-bis(4-(4-bromostyryl)styryl)benzene (**7.6**)

To a solution of KO*t*-Bu (0.84g, 7.5 mmol, 280 mol%) in anhydrous THF (75 mL) cooled to 0 ˚C was added Wittig reagent (3.07 g, 6.0 mmol, 240 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of dialdehyde **S7.4** (1.34 g, 10.0 mmol, 100 mol%) in THF (75 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (25 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (short plug, SiO_2; hexanes) to furnish the title compound **7.2c** (1.08 g, 1.67 mmol, mixture of isomers) in 67% yield as a waxy yellow solid.

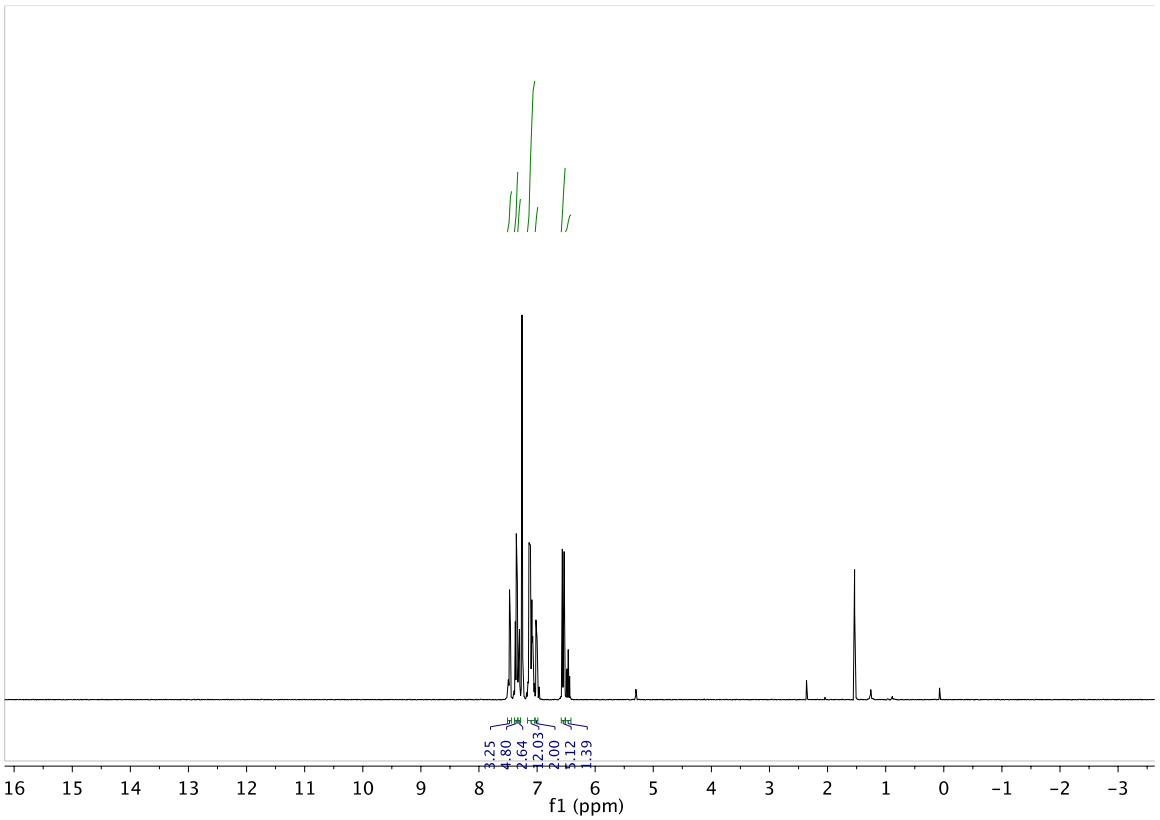
TLC (SiO_2): R_f = 0.67 (hexanes).

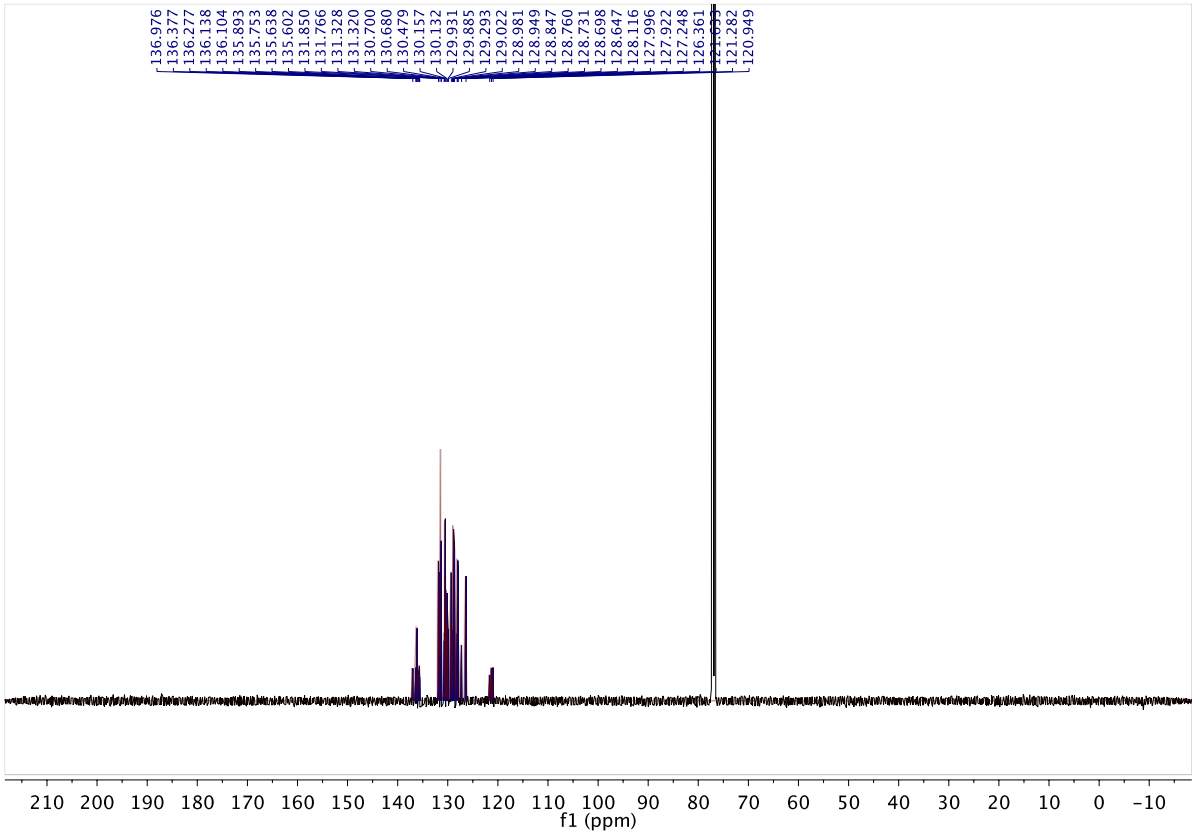
^{1}H NMR: (500 MHz, $CDCl_3$, diastereomeric mixture): δ = 7.48 (t, *J* = 7.9 Hz, 3H), 7.36 (t, *J* = 8.5 Hz, 4H), 7.31 (dd, *J* = 8.4, 3.7 Hz, 3H), 7.14-7.06 (m, 10 H), 7.03-6.99 (m, 2H), 6.55 (d, *J* = 15.3 Hz, 5H), 6.46 (t, *J* = 11.8 Hz, 1H) ppm.

^{13}C NMR: (125 MHz, $CDCl_3$, diastereomeric mixture) δ 137.0, 136.4, 136.3, 136.1, 136.1, 135.9, 135.8, 135.6, 135.6, 131.9, 131.8, 131.3, 131.3, 130.7, 130.7, 130.5, 130.2, 130.1, 129.9, 129.9, 129.3, 129.0, 128.98, 128.95, 128.85, 128.76, 128.73, 128.70, 128.65, 128.12, 128.00, 127.92, 127.25, 126.36, 121.6, 121.3, 121.0 ppm.

HRMS: (CI^+) Calculated for $C_{38}H_{28}Br_2[M^+]$ = 642.0558, Found 642.0560.

FTIR: (neat): 3015, 1484, 1070, 1009, 961, 880, 812, 754, 695 cm^{-1}.


3.25
4.80
2.64
12.03
2.00
5.12
1.39
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


136.976
136.377
136.277
136.138
136.104
135.893
135.753
135.638
135.602
131.850
131.766
131.328
131.320
130.700
130.680
130.479
130.157
130.132
129.931
129.885
129.293
129.022
128.981
128.949
128.847
128.760
128.731
128.698
128.647
128.116
127.996
127.922
127.248
126.361
121.282
120.949
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2,2'-(1,4-phenylene)bis(1-(4-(2-(4-bromophenyl)-1,2-dihydroxyethyl)phenyl)ethane-1,2-diol) (**7.8**)

To a solution of tetraene **7.6** (65 mg, 0.1 mmol, 100 mol%) in acetone (0.9 mL), chloroform (0.3 mL), and water (0.3 mL) was added NMO in water (w/w 50%) (94 mg, 0.4 mmol, 400 mol%). The mixture was allowed to stir for 50 min. Silica and ~100 mg of activated carbon was added to the reaction mixture, and volatiles were removed under vacuum. The resulting solids were loaded onto a column of silica and subjected to flash column chromatography (SiO_2; CH_2Cl_2: ethyl acetate = 1:1 to CH_2Cl_2: ethyl acetate: MeOH = 4:3:1) and then triterated with Et_2O to furnish the title compound **7.8** (35 mg, 0.045 mmol) in 45% yield as a gray solid.

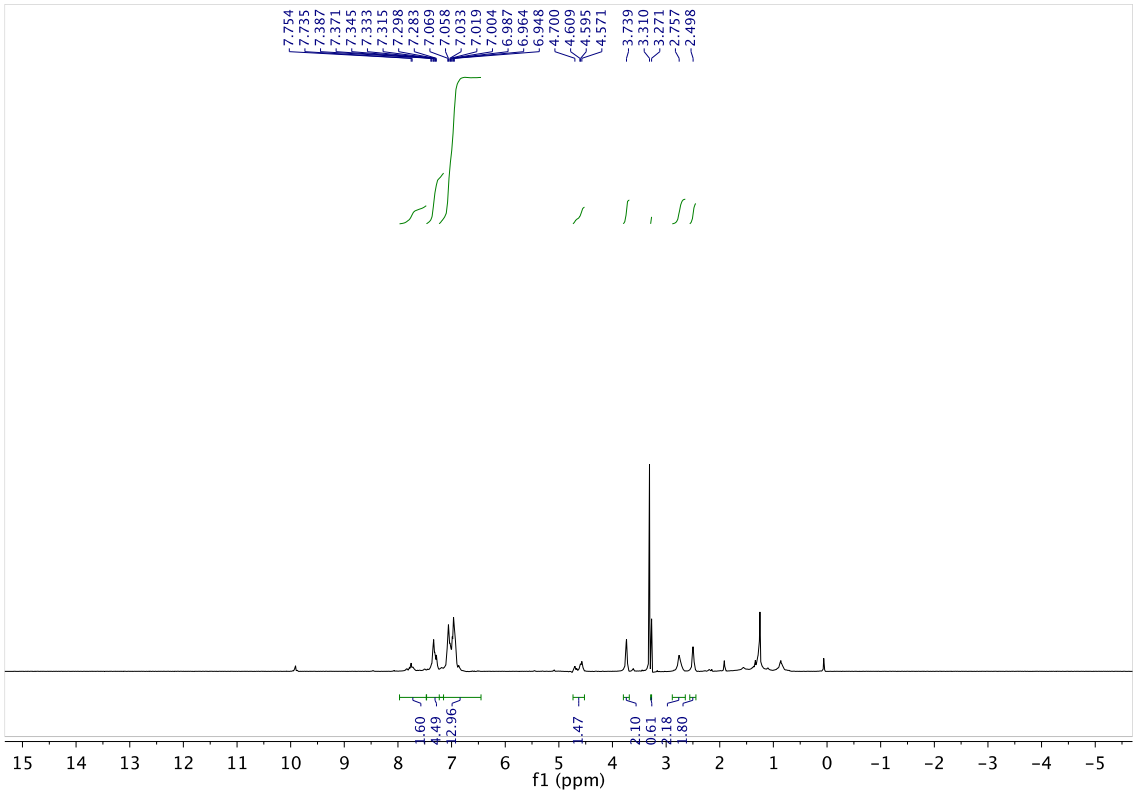
TLC (SiO_2): R_f = 0.30, 0.25 (inseparable isomers, CH_2Cl_2: ethyl acetate: MeOH = 4:3:1).

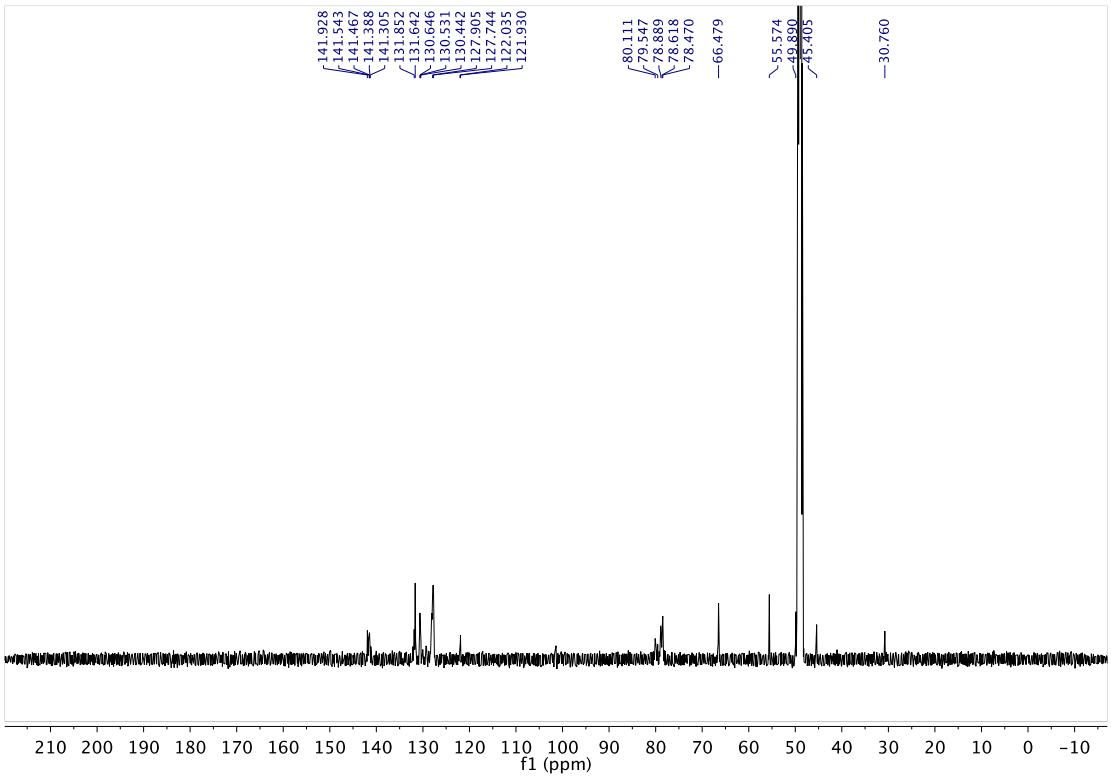
^{1}H NMR: (500 MHz, CD_3OD, water suppression, mixtures of isomers): δ = 7.85-7.67 (m, 2H), 7.41-7.42 (m, 5H), 7.13-6.84 (m, 13H), 4.74-4.52 (m, 1.5H), 3.74 (s, 2H), 3.27 (s, 0.5 H), 2.76 (s, 2H), 2.50 (s, 2H) ppm.

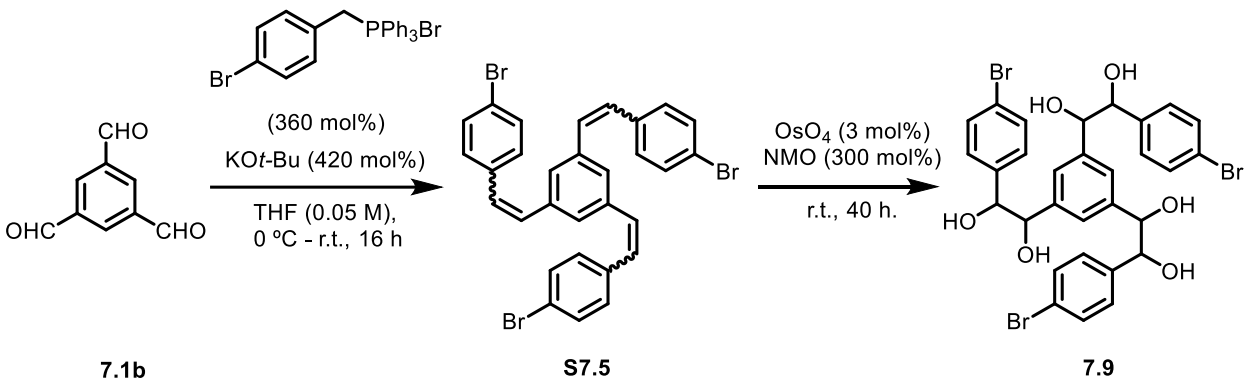
^{13}C NMR: (125 MHz, CD_3OD, mixture of isomers): δ = 141.9, 141.5, 141.5, 141.4, 141.3, 131.9, 131.6, 130.7, 130.5, 130.4, 127.9, 127.7, 122.0, 121.9, 80.1, 79.6, 78.9, 78.6, 78.5, 66.5, 55.6, 49.9, 45.4, 30.8 ppm.

HRMS: (ESI^+) Calculated for $C_{38}H_{36}Br_2O_8$ $[M+Na^+]$ = 801.0669, Found 801.0661.

FTIR: (neat): 3370, 2389, 1045, 895, 678 cm^{-1}.


7.754
7.735
7.387
7.371
7.345
7.333
7.315
7.298
7.283
7.069
7.058
7.033
7.019
7.004
6.987
6.964
6.948
4.700
4.609
4.595
4.571
3.739
3.310
3.271
2.757
2.498
1.60
4.49
12.96
1.47
2.10
0.61
2.18
1.80
f1 (ppm)


141.928
141.543
141.467
141.388
141.305
131.852
131.642
130.646
130.531
130.442
127.905
127.744
122.035
121.930
80.111
79.547
78.889
78.618
78.470
66.479
55.574
49.890
45.405
30.760
f1 (ppm)



7.1b **S7.5** **7.9**

Benzene-1,3,5-tricarboxaldehyde **S7.5** was synthesized according to known procedures[34] and their characterization data match our own in all respects.

Synthesis of triene **S7.5** from dialdehyde **7.9**:

To a solution of KO*t*-Bu (4.72 g, 42.0 mmol, 420 mol%) in anhydrous THF (100 mL) cooled to 0 ˚C was added phosphonium salt (18.4 g, 36.0 mmol, 360 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of tricarbonyl **7.1b** (1.62 g, 10.0 mmol, 100 mol%) in THF (100 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 99:1 to 98:2) to furnish the title compound **7.9** (4.41 g, 7.1 mmol) in 71% yield as a yellow solid.

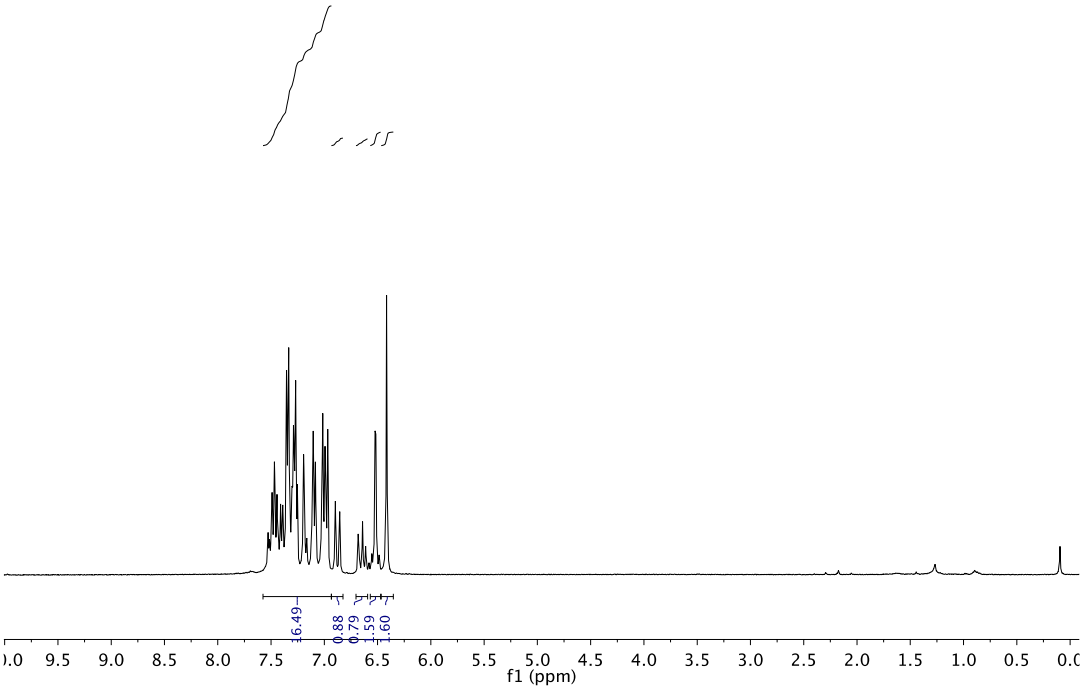
TLC (SiO_2): R_f = 0.73 (hexanes : ethyl acetate = 90:10).

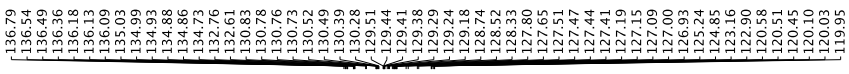
^{1}H NMR: (400 MHz, $CDCl_3$, 3 diastereomers): δ = 7.53–6.86 (m, 17H), 6.66–6.42 (m, 4H) ppm.

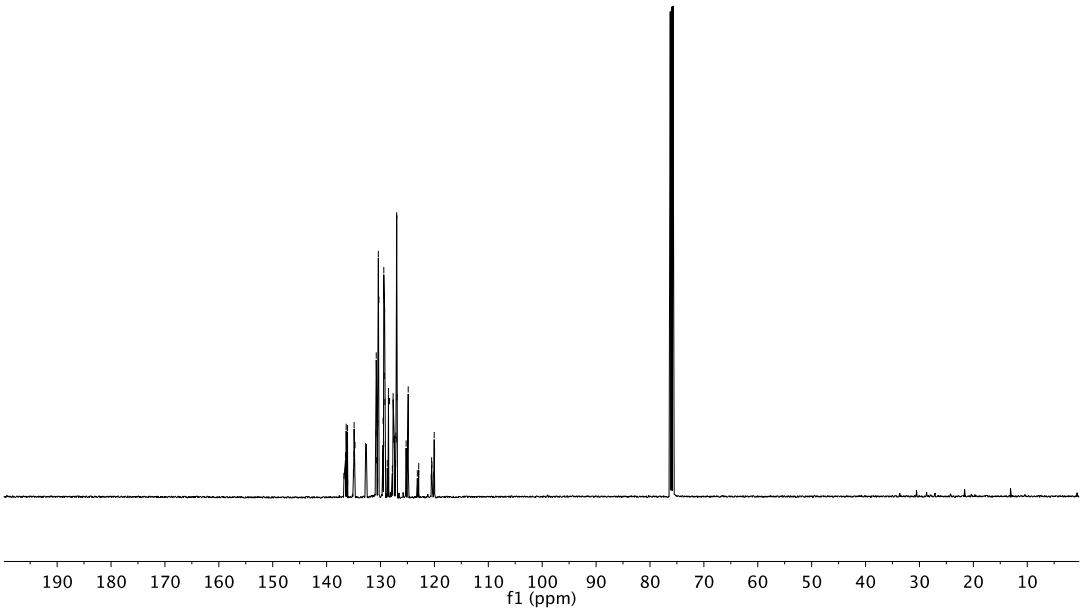
^{13}C NMR: (100 MHz, $CDCl_3$, 3 diastereomers): δ = 136.8, 136.5, 136.5, 136.4, 136.2, 136.1, 136.1, 135.0, 135.0, 134.9, 134.9, 134.9, 134.7, 132.8, 132.6, 120.8, 130.8, 130.8, 130.7, 130.5, 130.5, 130.4, 130.3, 129.5, 129.4, 129.4, 129.4, 129.3, 129.2, 129.2, 128.7, 128.5, 128.3, 127.8, 127.7, 127.5, 127.5, 127.4, 127.4, 127.2, 127.2, 127.1, 127.0, 126.9, 125.2, 124.9, 123.2, 122.9, 120.6, 120.5, 120.5, 120.1, 120.0, 120.0 ppm.

HRMS: (CI) Calculated for $C_{30}H_{21}Br_3$ [M^+] = 621.9173, Found 621.9167.

FTIR: (neat): 3012, 2692, 1485, 1071, 1009 cm^{-1}.


16.49
0.88
0.79
1.59
1.60
f1 (ppm)


136.79
136.54
136.49
136.36
136.18
136.13
136.09
135.03
134.99
134.93
134.88
134.86
134.73
132.76
132.61
130.83
130.78
130.76
130.73
130.52
130.49
130.39
130.28
129.51
129.44
129.41
129.38
129.29
129.24
129.18
128.74
128.52
128.33
127.80
127.65
127.51
127.47
127.44
127.41
127.19
127.15
127.09
127.00
126.93
125.24
124.85
123.16
122.90
120.58
120.51
120.45
120.10
120.03
119.95


f1 (ppm)

Synthesis of tris diol **7.9** from triene:

To a solution of triene **S7.5** (3.11 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (3.51 g, 15.0 mmol, 300 mol%). Then, OsO_4 (1.0 M in *t*-BuOH, 0.15 mL, 0.15 mmol, 3 mol%) was added. The mixture was allowed to stir for 40 hours. Toluene (30 mL) was added, and concentrated under vacuum. Recovered solid was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 50:50 to 20:80) to furnish the title compound **7.9** (1.84 g, 3.5 mmol) in 52% yield as a white solid. The material was characterized by ^{1}H NMR only.

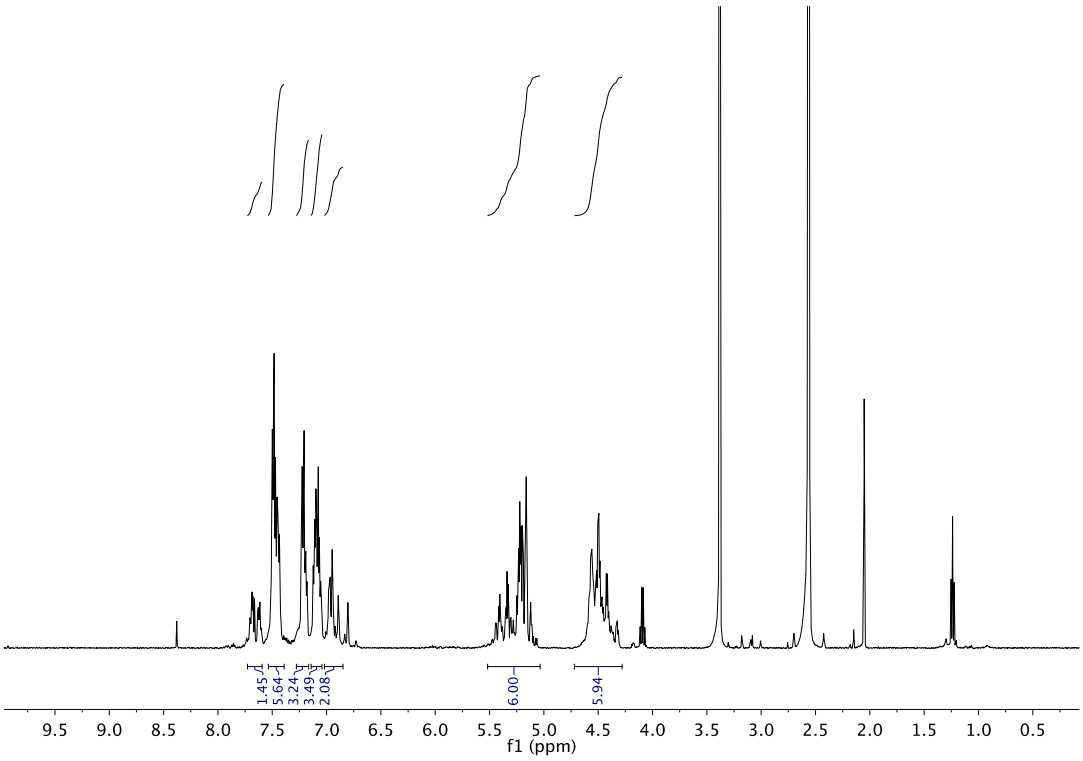
TLC (SiO_2): R_f = 0.42 (ethyl acetate : MeOH = 95:5).

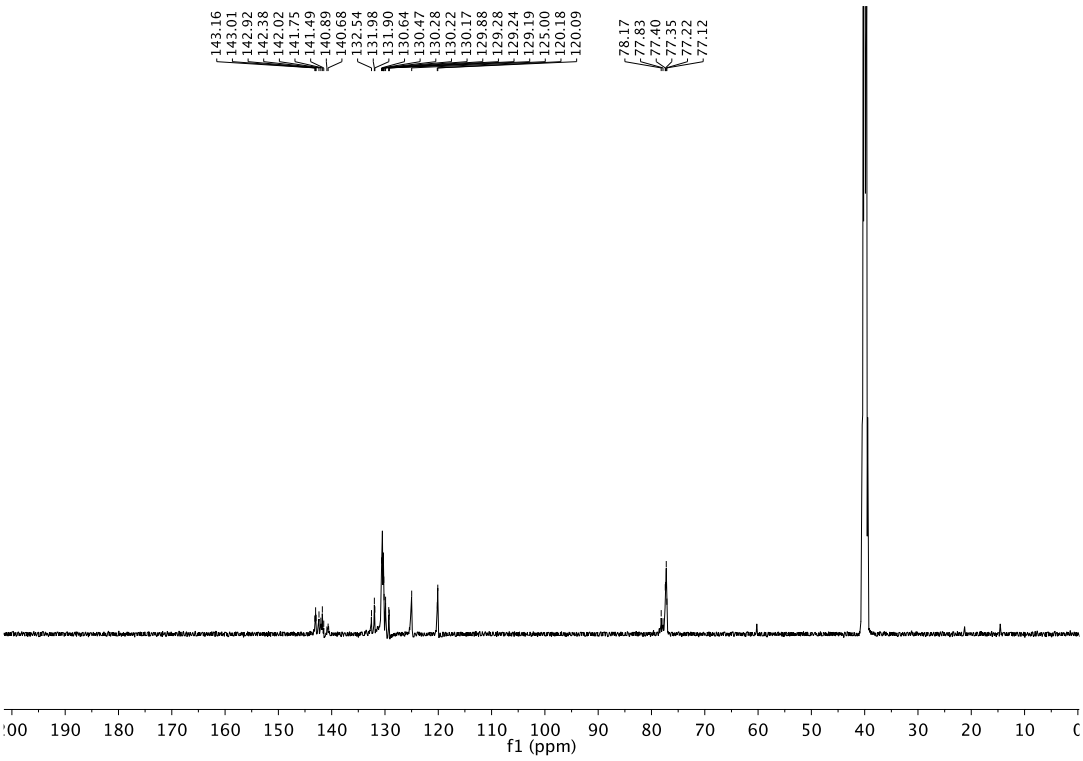
^{1}H NMR: (400 MHz, d_6-DMSO, 2 diastereomers): δ = 7.51–7.43 (m, 7H), 7.23–6.80 (m, 8H), 5.41–5.11 (m, 6H), 4.59–4.40 (m, 6H) ppm.

^{13}C NMR: (100 MHz, d_6-DMSO, 2 diastereomers): δ = 143.2, 143.0, 142.9, 142.4, 142.0, 141.8, 141.5, 140.9, 140.7, 132.5, 132.0, 131.9, 130.6, 130.5, 130.3, 130.2, 130.2, 129.9, 129.3, 129.2, 129.2, 125.0, 120.2, 120.1, 78.2, 77.8, 77.4, 77.4, 77.2, 77.1 ppm.

HRMS: (ESI) Calculated for $C_{30}H_{28}Br_2O_6$ $[M+H^+]$ = 667.0127, Found 667.0124.

FTIR: (neat): 2360, 2343, 1070, 1010cm^{-1}.


1.45
5.64
3.24
3.49
2.08
6.00
5.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


143.16
143.01
142.92
142.38
142.02
141.75
141.49
140.89
140.68
132.54
131.98
131.90
130.64
130.47
130.28
130.22
130.17
129.88
129.28
129.24
129.19
125.00
120.18
120.09
78.17
77.83
77.40
77.35
77.22
77.12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Synthesis and Characterization of Cycloadducts and Oligophenylenes 7.10a-c, 7.11, 7.12, and 7.13

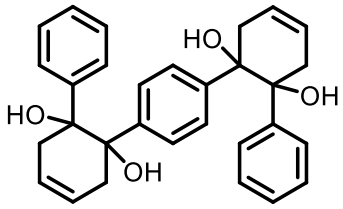
Ruthenium catalyzed cycloaddition reactions

A resealable pressure tube (ca. 13 x 100 mm) was charged with $[Ru_3(CO)_{12}]$ (2.7 mg, 0.004 mmol, 2 mol%), dppp (4.8 mg, 0.012 mmol, 6 mol%), 3,5-Me_2BzOH (3.0 mg, 0.02 mmol, 10 mol%), polyol (0.2 mmol, 100 mol). The pressure tube was purged with argon and toluene/dimethylacetamide (1:1, 0.40 mL) was added via syringe, followed by freshly condensed butadiene (0.17 mL, 2.0 mmol, 1000 mol%; or 5 equivalents per diol). The septum was replaced with a screw cap, and the reaction was placed in a 130 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature The volatiles were removed *in vacuo* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired products.

Dehydration reactions with *p*-toluenesulfonic acid

A resealable pressure tube (ca. 13 x 100 mm) was charged with cycloadduct (0.2 mmol, 100 mol%) followed by *p*-toluenesulfonic acid (3.8 mg, 0.02 mmol, 10 mol%). The pressure tube was purged with argon and toluene (2.9 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in a 75 ˚C oil bath. After 40 hours, the reaction vessels was removed from the oil bath and allowed to cool to room temperature. The volatiles were removed *in vacuo,* and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the desired product **7.10a-c**, **7.11-7.13**.

3',3''',6',6'''-tetrahydro-[1,1':2',1'':4'',1''':2''',1''''-quinquephenyl]-1',1''',2',2'''-tetraol (S7.6)



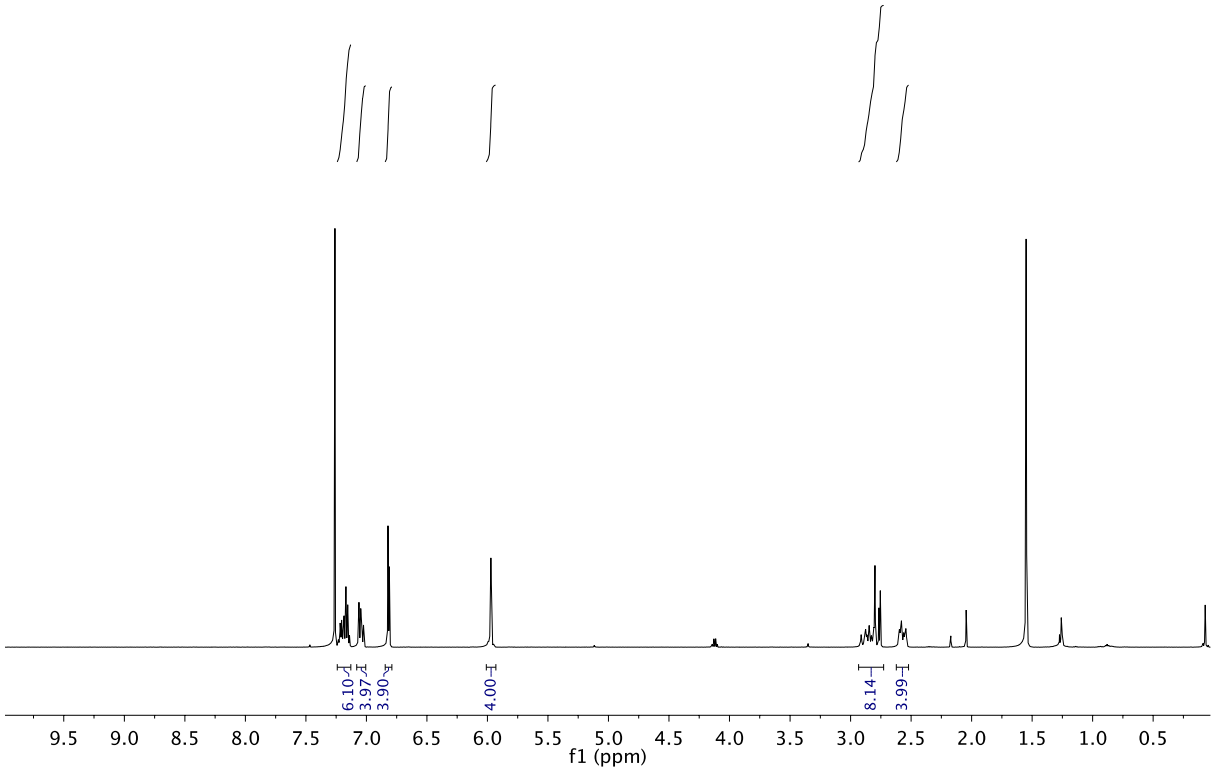
The reaction was conducted with bis diol **7.10a** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate =80:20 to 50:50) provided the title compound **S7.6** (64.5 mg, 0.18 mmol) in 82% yield as a white solid.

TLC (SiO_2): R_f = 0.25 (hexanes : ethyl acetate = 50:50).

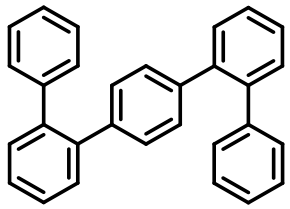
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.24–7.13 (m, 6H), 7.07–7.01 (m, 4H), 6.01–5.93 (m, 4H), 2.93–2.74 (m, 8H), 2.62–2.52 (m, 4H) ppm.

HRMS: (ESI) Calculated for $C_{30}H_{30}O_4$ [M+Na^+] = 477.2036, Found 477.2044.

FTIR: (neat): 2365, 1739, 1366, 1217 cm^{-1}.


6.10
3.97
3.90
4.00
8.14
3.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (7.10a)



The reaction was conducted with cycloadduct **S7.6** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:DCM = 90:10) provided the title compound **7.10a** (57.4 mg, 0.14 mmol) in 75% yield as a white solid. The NMR spectra were consistent with a literature report.

TLC (SiO_2): R_f = 0.30 (hexanes : DCM = 90:10).

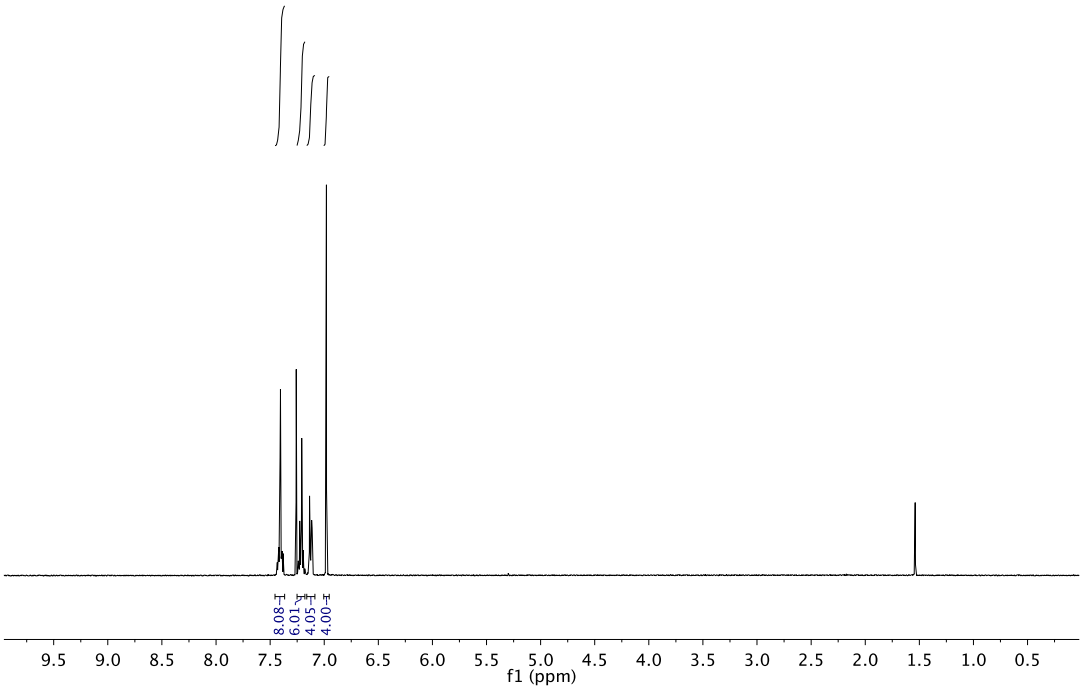
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 8H), 7.23–7.20 (m, 6H), 7.14–7.11 (m, 4H), 6.98 (s, 4H) ppm.

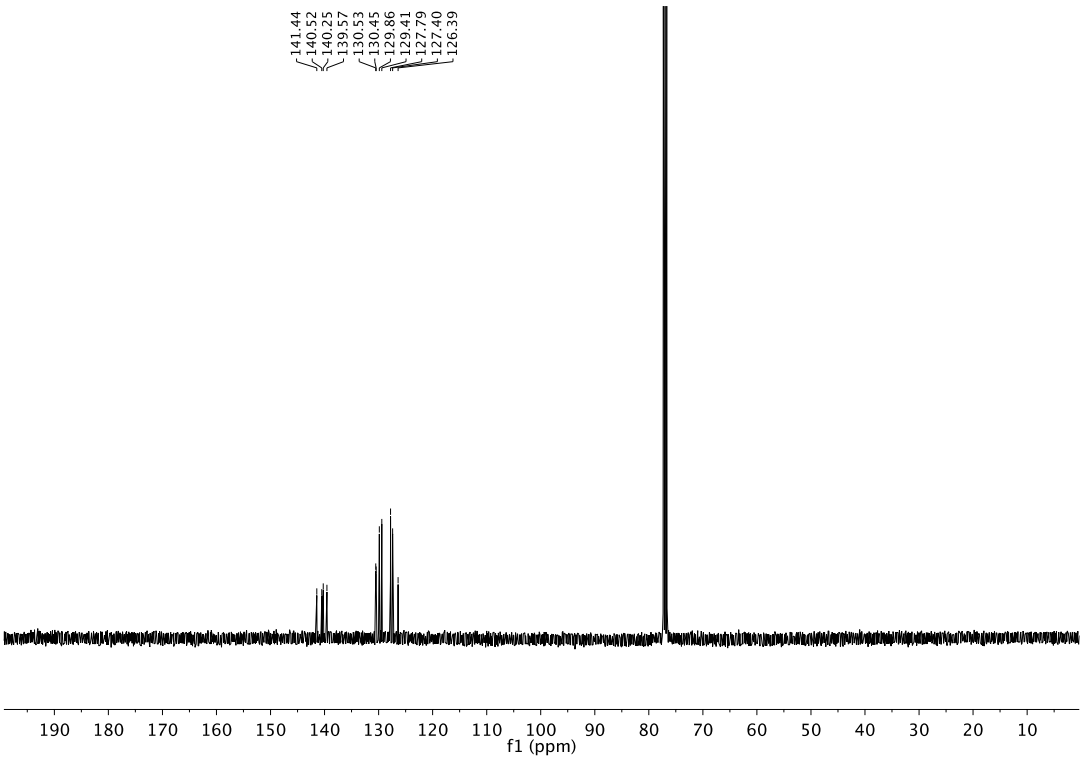
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 141.4, 140.5, 140.3, 139.6, 130.5, 130.5, 129.9, 129.4, 127.8, 127.4, 126.4 ppm.

MP: 189 – 191 °C.

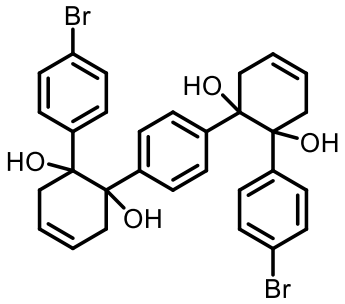
HRMS: (CI) Calculated for $C_{30}H_{22}$ [M^+] = 382.1722, Found 382.1722.

FTIR: (neat): 2922, 2854, 1114, 965 cm^{-1}.


8.08
6.01
4.05
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


141.44
140.52
140.25
139.57
130.53
130.45
129.86
129.41
127.79
127.40
126.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

4,4''''-dibromo-3',3''',6',6'''-tetrahydro-[1,1':2',1'':4'',1''':2''',1''''-quinquephenyl]-1',1''',2',2'''-tetraol (S7.7)



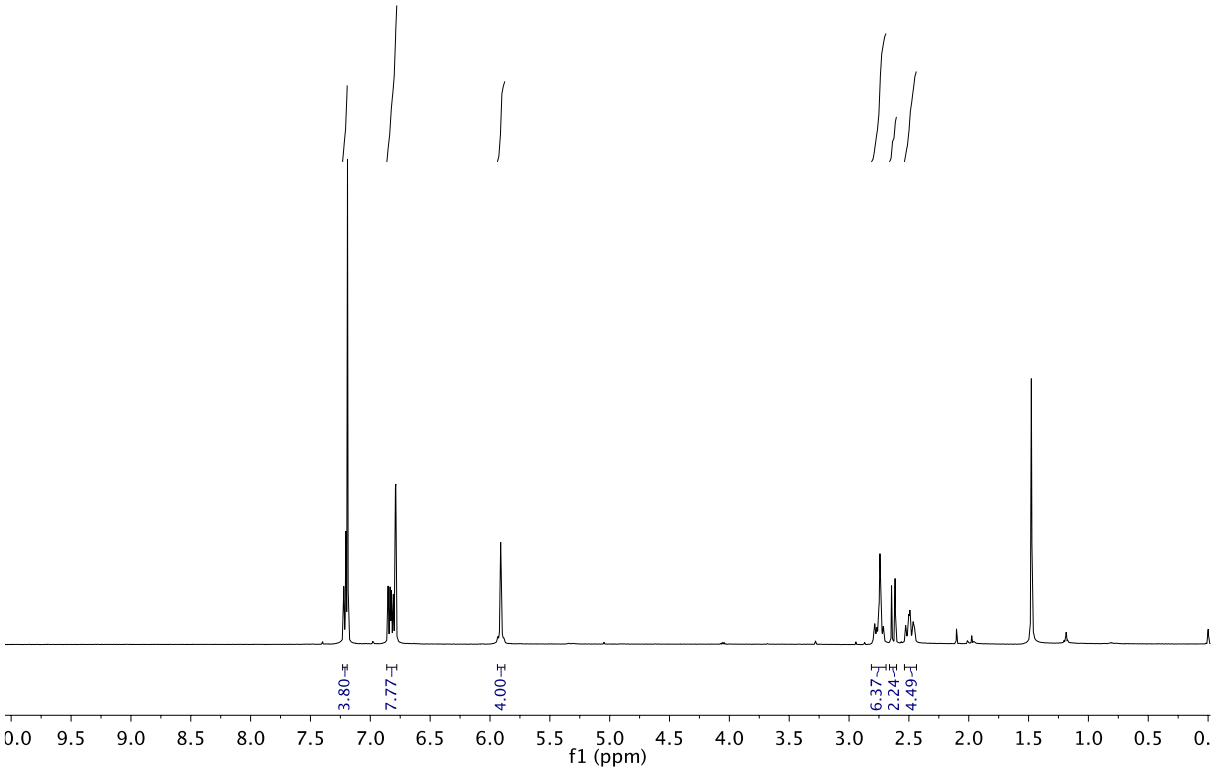
The reaction was conducted with bis diol **7.3b** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate =80:20 to 50:50) provided the title compound **S7.7** (107.7 mg, 0.18 mmol) in 88% yield as a white solid.

TLC (SiO_2): R_f = 0.25 (hexanes : ethyl acetate = 50:50).

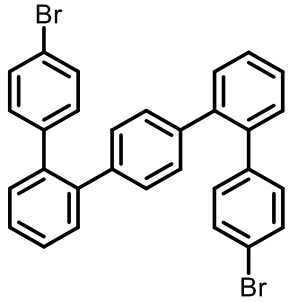
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 4H), 46.93–6.84 (m, 8H), 6.01–5.94 (m, 4H), 2.87–2.50 (m, 12H) ppm.

HRMS: (ESI) Calculated for $C_{30}H_{28}Br_2O_6$ [M+Na^+] =635.0229, Found 635.0237.

FTIR: (neat): 3445, 2918, 763, 719 cm^{-1}.


3.80
7.77
4.00
6.37
2.24
4.49
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

4,4''''-dibromo-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl



The reaction was conducted with cycloadduct **S7.7** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:DCM = 90:10) provided the title compound **7.10b** (92.9 mg, 0.17 mmol) in 86% yield as a white solid.

TLC (SiO_2): R_f = 0.36 (hexanes : DCM = 90:10).

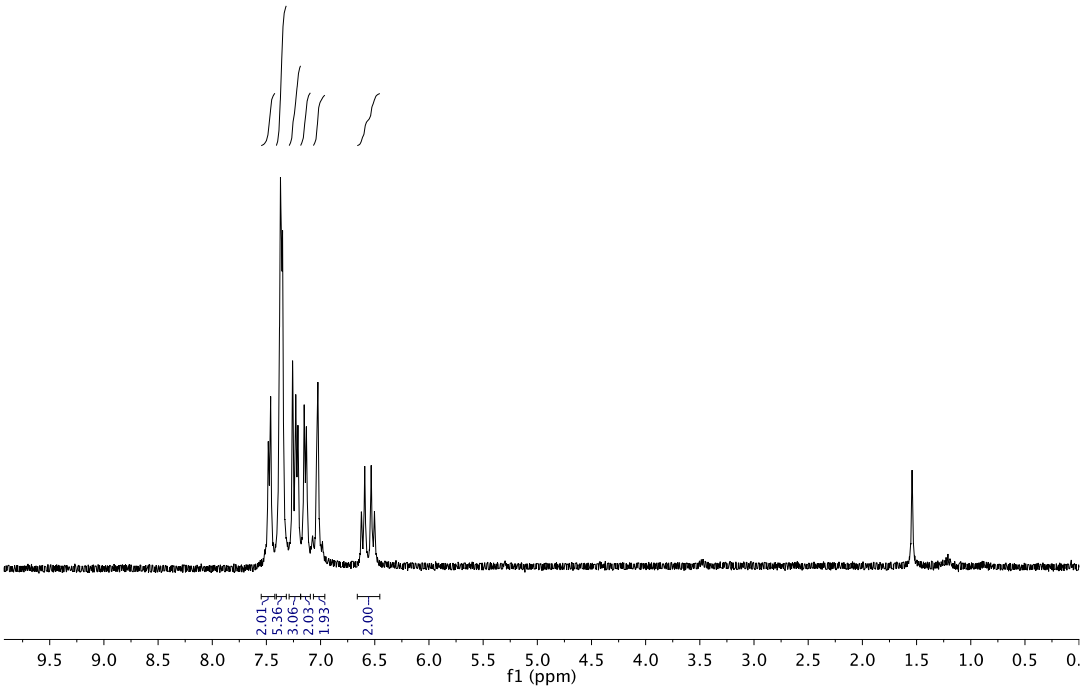
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.42–7.34 (m, 12H), 7.01–6.99 (m, 8H) ppm.

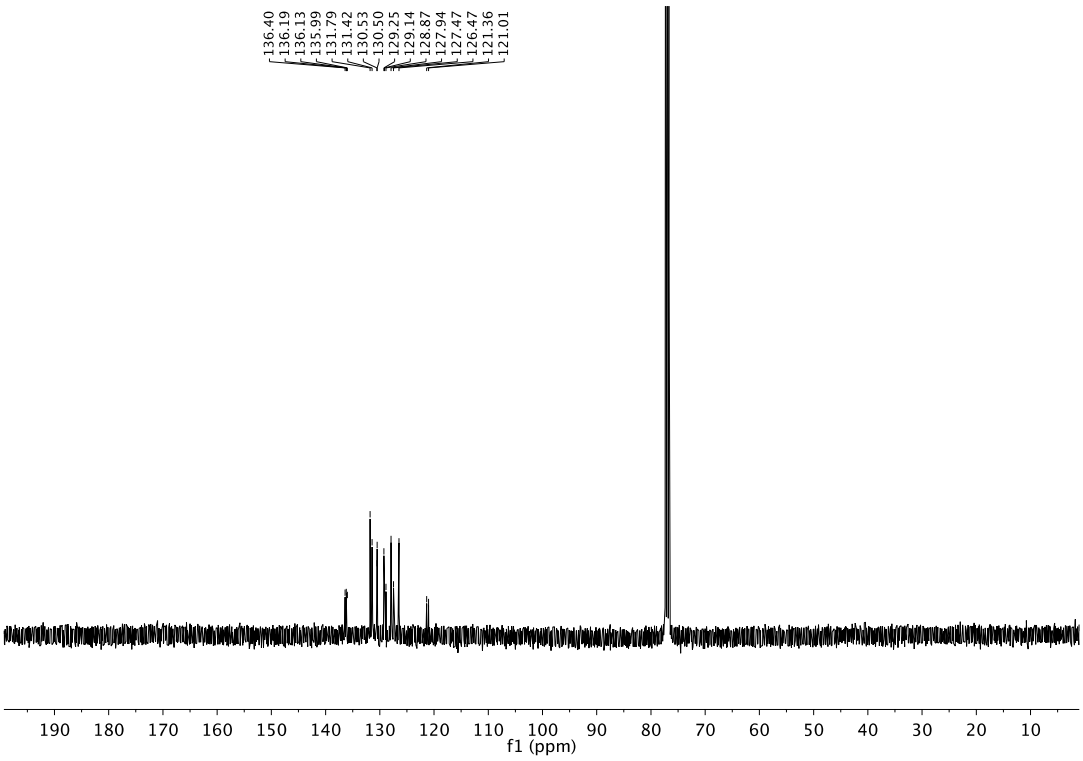
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 140.4, 140.0, 139.5, 139.2, 131.5, 131.0, 130.6, 130.4, 129.5, 127.8, 127.6, 120.9 ppm.

MP: 232 – 235 °C.

HRMS: (CI^+) Calculated for $C_{30}H_{20}Br_2$ [M^+] = 539.9911, Found 539.9915.

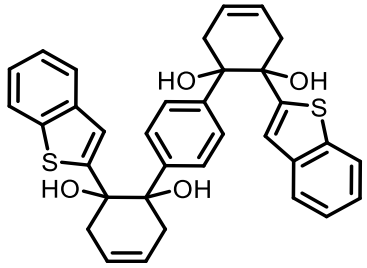
FTIR: (neat): 1468, 1001, 827, 752 cm^{-1}.


2.01
5.36
3.06
2.03
1.93
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


136.40
136.19
136.13
135.99
131.79
131.42
130.53
130.50
129.25
129.14
128.87
127.94
127.47
126.47
121.36
121.01
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2,2''-bis(benzo[*b*]thiophen-2-yl)-3,3'',6,6''-tetrahydro-[1,1':4',1''-terphenyl]

1,1'',2,2''(2*H*,2''*H*)-tetraol (S7.8)



The reaction was conducted with bis diol **7.3c** in accordance with the general procedure in 2.0 mL toluene/DMA = 1:1 (0.1 M). Flash column chromatography (SiO_2, hexanes:ethyl acetate = 50:50) provided the title compound **S7.8** (89.5 mg, 0.16 mmol) in 79% yield as a white solid.

TLC (SiO_2): R_f = 0.29 (hexanes : ethyl acetate = 1:2).

^{1}H NMR: (400 MHz, $CDCl_3$, one isomer) δ 7.71 - 7.68 (m, 2H), 7.57 - 7.53 (m, 2H), 7.30 - 7.24 (m, 4H), 7.02 (s, 4H), 6.72 (s, 2H), 5.99 (d, J = 10.2 Hz, 2H), 5.87 (d, J = 10.2 Hz, 2H), 3.03 - 2.63 (m, 12H) ppm.

^{13}C NMR: (100 MHz, $CDCl_3$, one isomer) δ 147.7, 141.1, 139.3, 139.2, 126.7, 125.6, 125.6, 124.7, 124.0, 123.9, 123.3, 121.9, 121.4, 77.2, 76.9, 39.5, 39.4 ppm

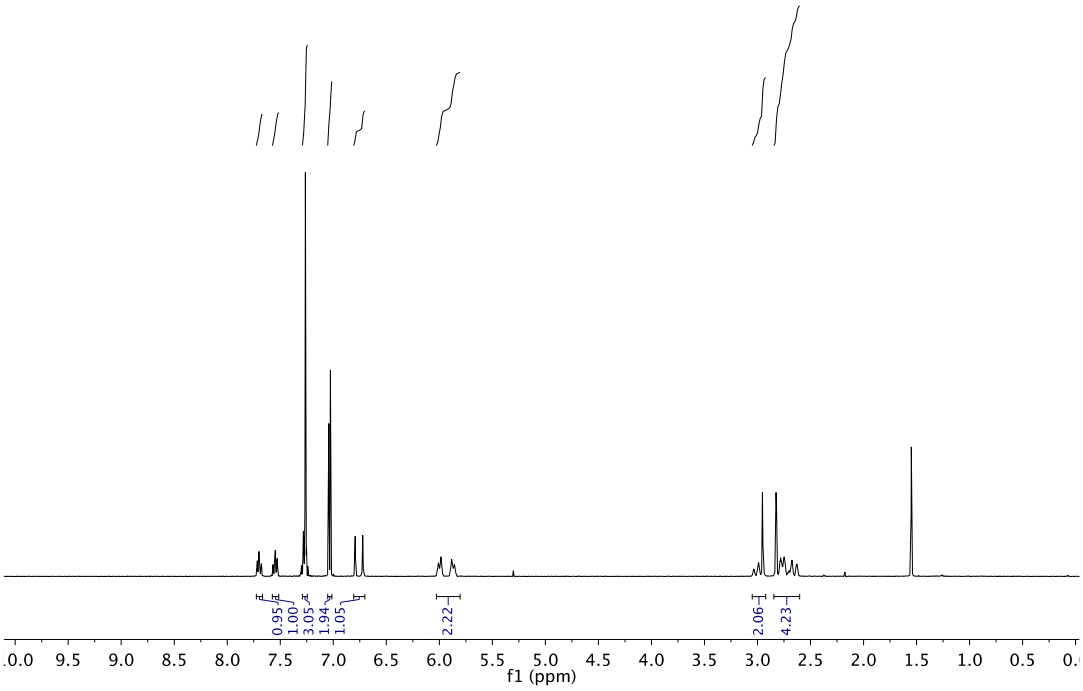
^{1}H NMR: (400 MHz, CDCl3, the other isomer) δ 7.71 - 7.68 (m, 2H), 7.57 - 7.53 (m, 2H), 7.30 - 7.24 (m, 4H), 7.04 (s, 4H), 6.79 (s, 2H), 5.99 (d, J = 10.2 Hz, 2H), 5.87 (d, J = 10.2 Hz, 2H), 3.03 - 2.63 (m, 12H) ppm.

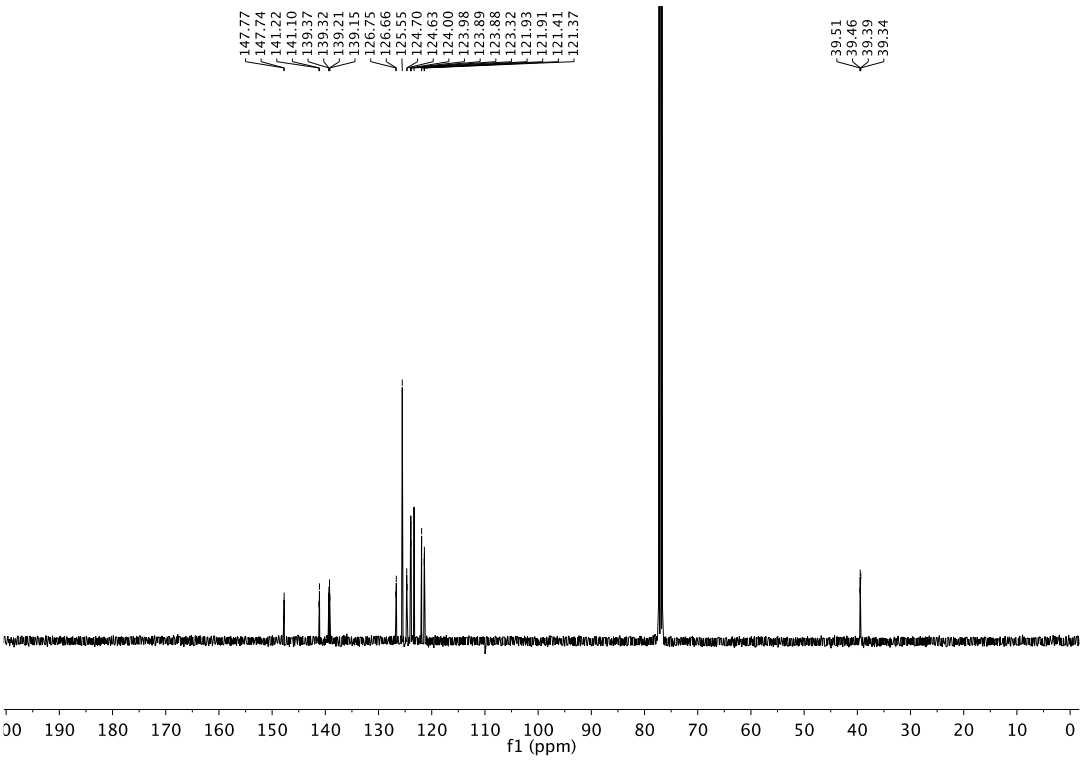
^{13}C NMR: (100 MHz, $CDCl_3$, the other isomer) δ 147.8, 141.2, 139.4, 139.2, 126.8, 125.6, 125.6, 124.6, 124.0, 123.9, 123.3, 122.0, 121.4, 77.2, 76.8, 39.5, 39.4 ppm

MP: 122-148 °C

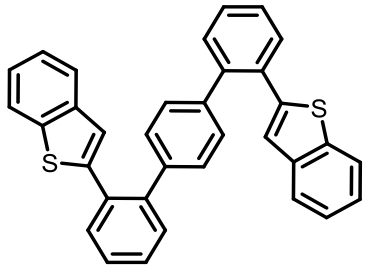
HRMS: (ESI) Calculated for $C_{34}H_{30}O_4S_2$ [M+Na^+] =589.14780, Found 589.14770.

FTIR: (neat) 3497, 3367, 3056, 3025, 2915, 1509, 1434, 1042, 974, 831, 746, 725 cm^{-1}


0.95
1.00
3.05
1.94
1.05
2.22
2.06
4.23
f1 (ppm)


147.77
147.74
141.22
141.10
139.37
139.32
139.21
139.15
126.75
126.66
125.55
124.70
124.63
124.00
123.98
123.89
123.88
123.32
121.93
121.91
121.41
121.37
39.51
39.46
39.39
39.34
f1 (ppm)

2,2''-bis(benzo[*b*]thiophen-2-yl)-1,1':4',1''-terphenyl (7.10c)



The reaction was conducted with cycloadduct **S7.8** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:DCM = 80:20) provided the title compound **7.10c** (72.2 mg, 0.15 mmol) in 73% yield as a white solid.

TLC (SiO_2): R_f = 0.79 (hexanes : DCM = 4:1).

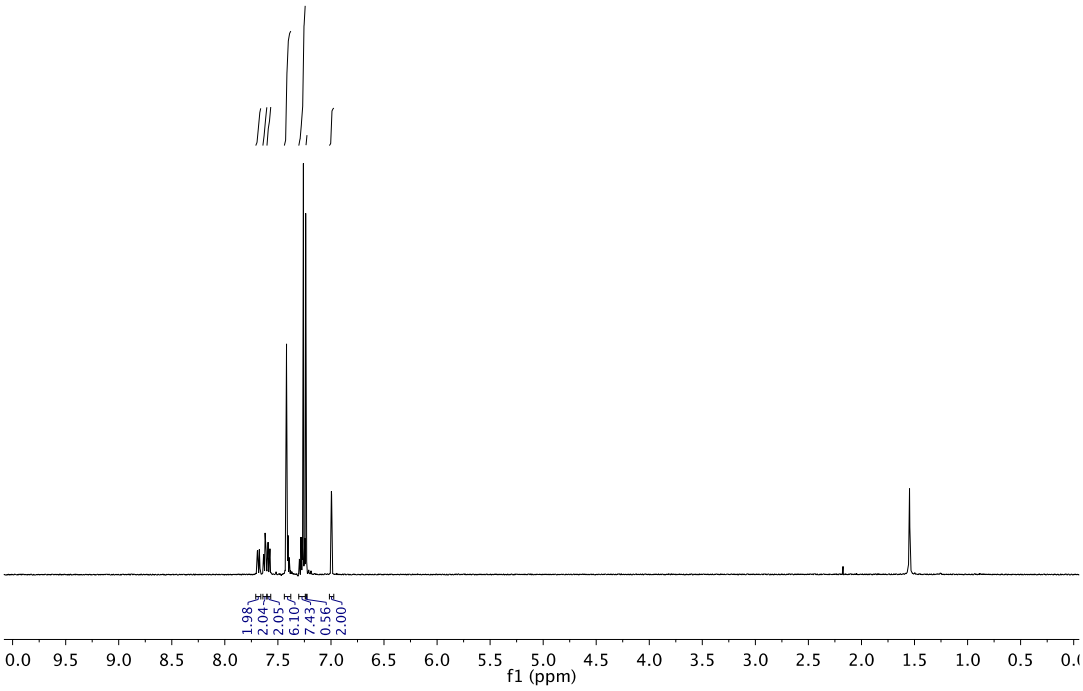
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.71 (d, J = 7.0 Hz, 2H), 7.66 - 7.63 (m, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.45 - 7.41 (m, 2H), 7.44 (s, 4H), 7.32 - 7.25 (m, 8H), 7.02 (s, 2H) ppm.

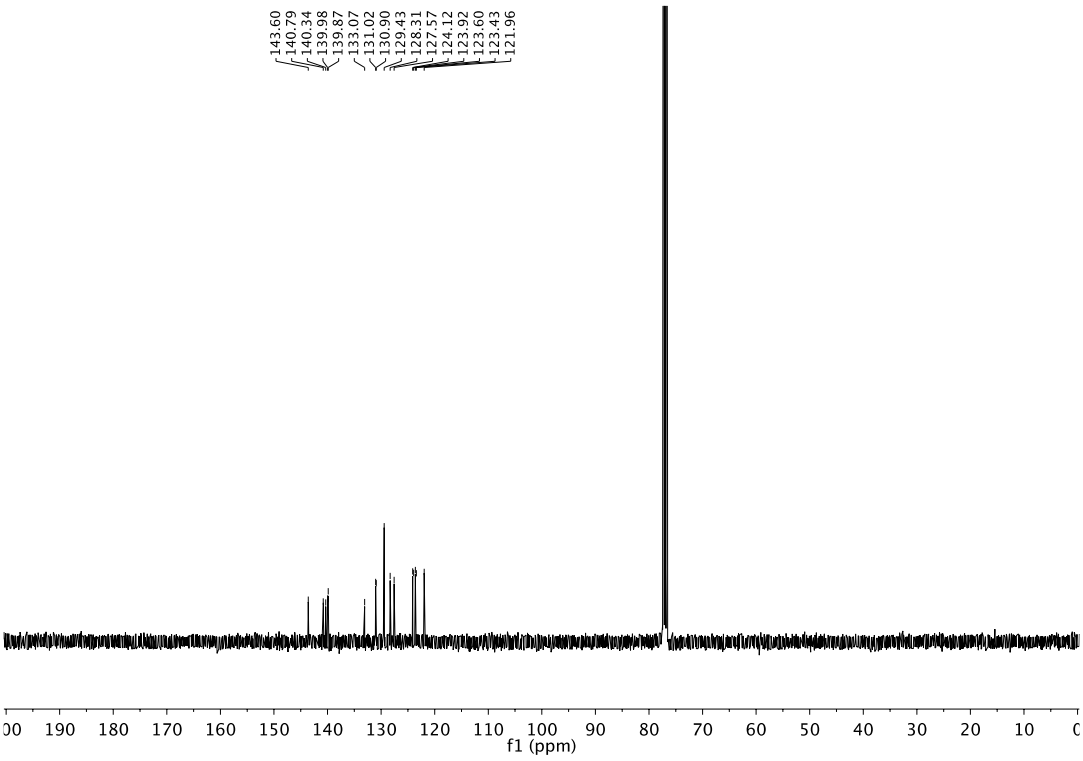
^{13}C NMR: δ 143.6, 140.8, 140.4, 140.0, 139.9, 133.1, 131.0, 130.9, 129.4, 129.4, 128.3, 127.6, 124.1, 123.9, 123.6, 123.4, 122.0 ppm.

MP: 197-198 °C

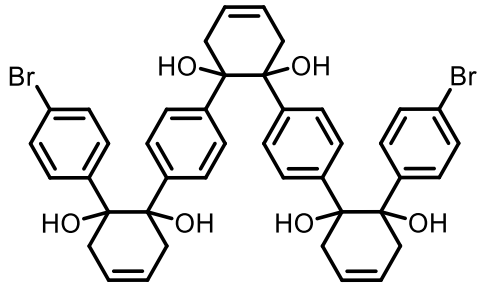
HRMS: (CI^+) Calculated for $C_{34}H_{22}S_2$ [M^+] =494.1163, Found 494.1163.

FTIR: 3053, 2980, 1472, 1432, 1004, 867, 743, 680 cm^{-1}.


1.98
2.04
2.05
6.10
7.43
0.56
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


143.60
140.79
140.34
139.98
139.87
133.07
131.02
130.90
129.43
128.31
127.57
124.12
123.92
123.60
123.43
121.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

4,4''''''-dibromo-3',3''',3''''',6',6''',6''''''-hexahydro [1,1':2',1'':4'',1''':2''',1'''':4'''',1''''':2''''',1''''''- sepiphenyl]- 1',1''',1''''', 2',2''',2''''''-hexaol (S7.9)



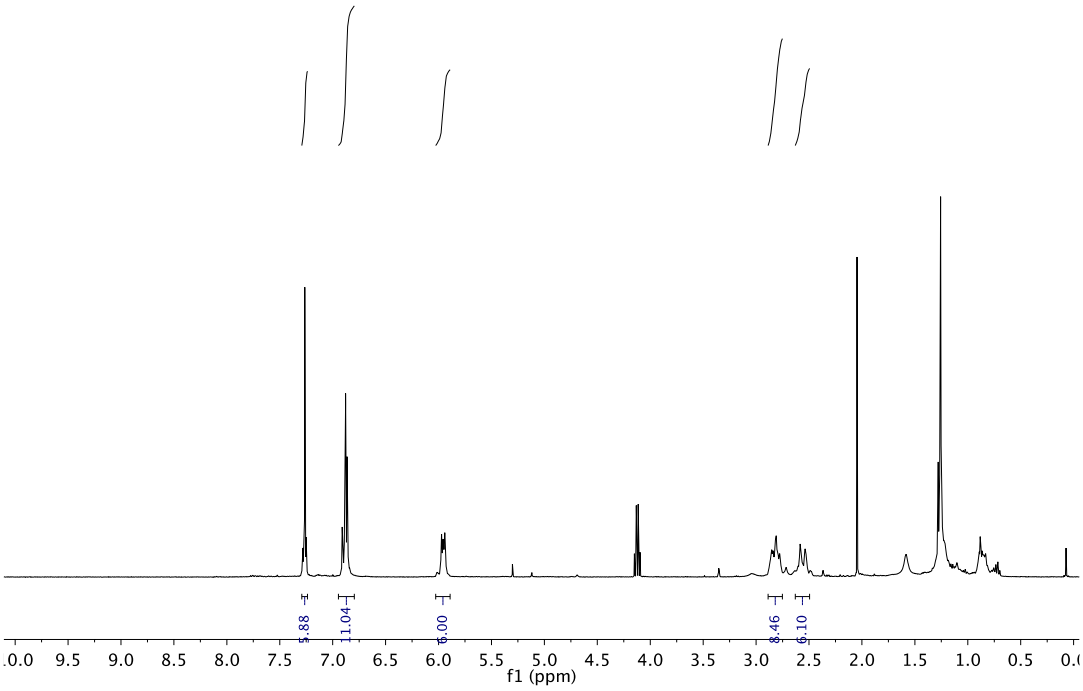
The reaction was conducted with tris diol **7.7** at 140 ˚C in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate =80:20 to 50:50) provided the title compound **S7.9** (145.7 mg, 0.18 mmol) in 91% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (hexanes : ethyl acetate = 60:40).

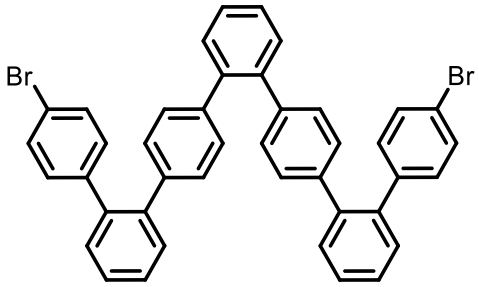
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.29–7.24 (m, 5H), 6.94–6.79 (m, 11H), 6.02–5.88 (m, 6H), 2.89–2.49 (m, 14H) ppm.

HRMS: (ESI) Calculated for $C_{42}H_{40}Br_2O_6$ [M+NH_4^+] =818.1501, Found 818.1514.

FTIR: (neat): 3430, 1365, 1216, 824 cm^{-1}.


5.88
11.04
6.00
8.46
6.10
f1 (ppm)

4,4''''''-dibromo-1,1':2',1'':4'',1''':2''',1'''':4'''',1''''':2''''',1''''''-sepiphenyl (7.11)



The reaction was conducted with cycloadduct **S7.9** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:DCM = 90:10) provided the title compound **7.11** (52.8 mg, 0.14 mmol) in 69% yield as a white solid.

TLC (SiO_2): R_f = 0.32 (hexanes : DCM = 90:10).

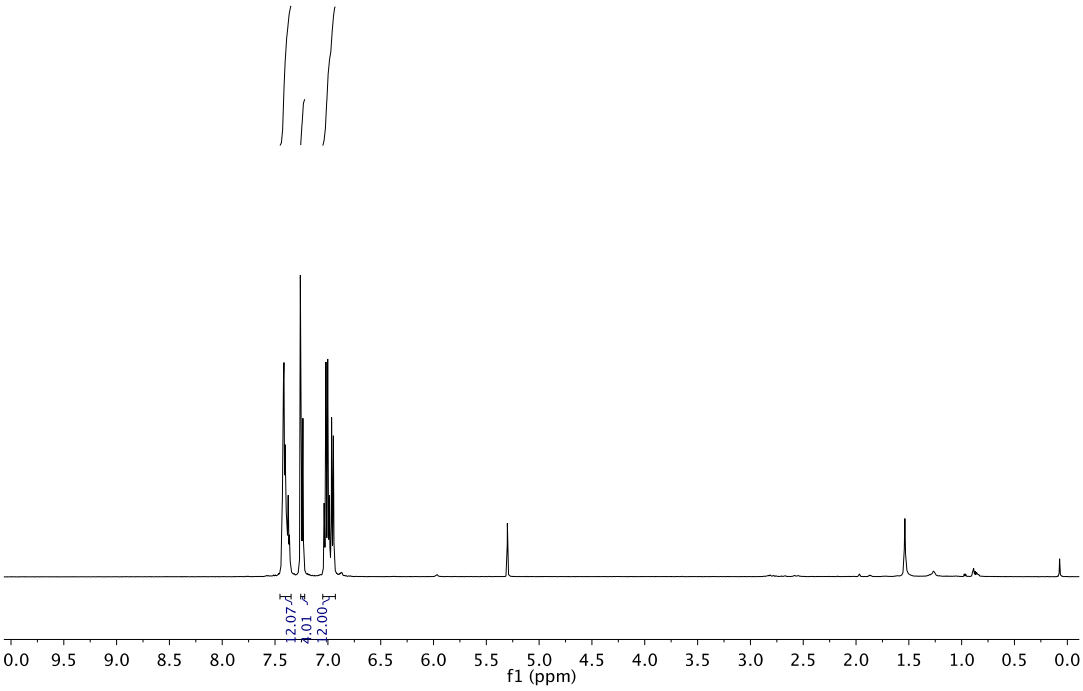
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.44–7.36 (m, 12H), 7.26–7.24 (q, 4H), 7.03–6.95 (m, 12H) ppm.

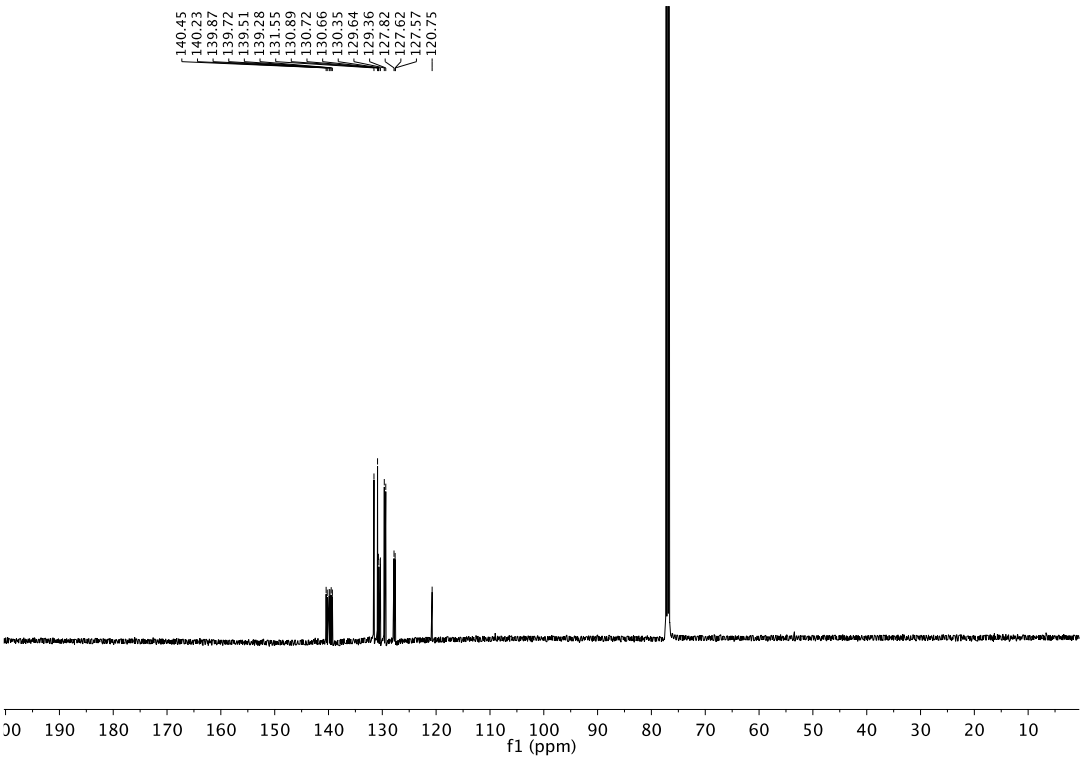
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 140.5, 140.2, 139.9, 139.7, 139.3, 139.5, 131.6, 130.9, 130.7, 130.7, 130.4, 129.6, 129.4, 127.8, 127.6, 127.6, 120.8 ppm.

MP: >250 °C.

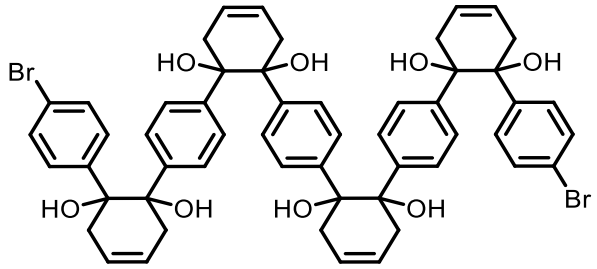
HRMS: (CI^+) Calculated for $C_{42}H_{28}Br_2$ [M+Na^+] = 692.0537, Found 692.0538.

FTIR: (neat): 1470, 1071, 824, 750 cm^{-1}.


12.07
4.01
12.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.45
140.23
139.87
139.72
139.51
139.28
131.55
130.89
130.72
130.66
130.35
129.64
129.36
127.82
127.62
127.57
120.75
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

4,4'''''''-dibromo-3',3''',3''''',3''''''',6',6''',6''''',6''''''-octahydro-[1,1':2',1'':4'',1''':2''',1'''':4'''',1''''':2''''',1''''':4''''',1''''':2''''',1'''''':2'''''',1''''''':2''''''',1'''''''-novemphenyl]-1',1''',1''''',1''''''', 2',2''',2''''',2''''''-octaol (S7.10)



The reaction was conducted with tetra(bis-diol) **7.8** in accordance with the general procedure, utilizing 39 mg, 0.05 mmol of **7.8**. Flash column chromatography (SiO_2, CH_2Cl_2: ethyl acetate = 50:50) provided the title compound **S7.10** (32 mg, 0.33 mmol) in 65% yield as an ecru solid. Some minor impurities (<5%) were inseparable.

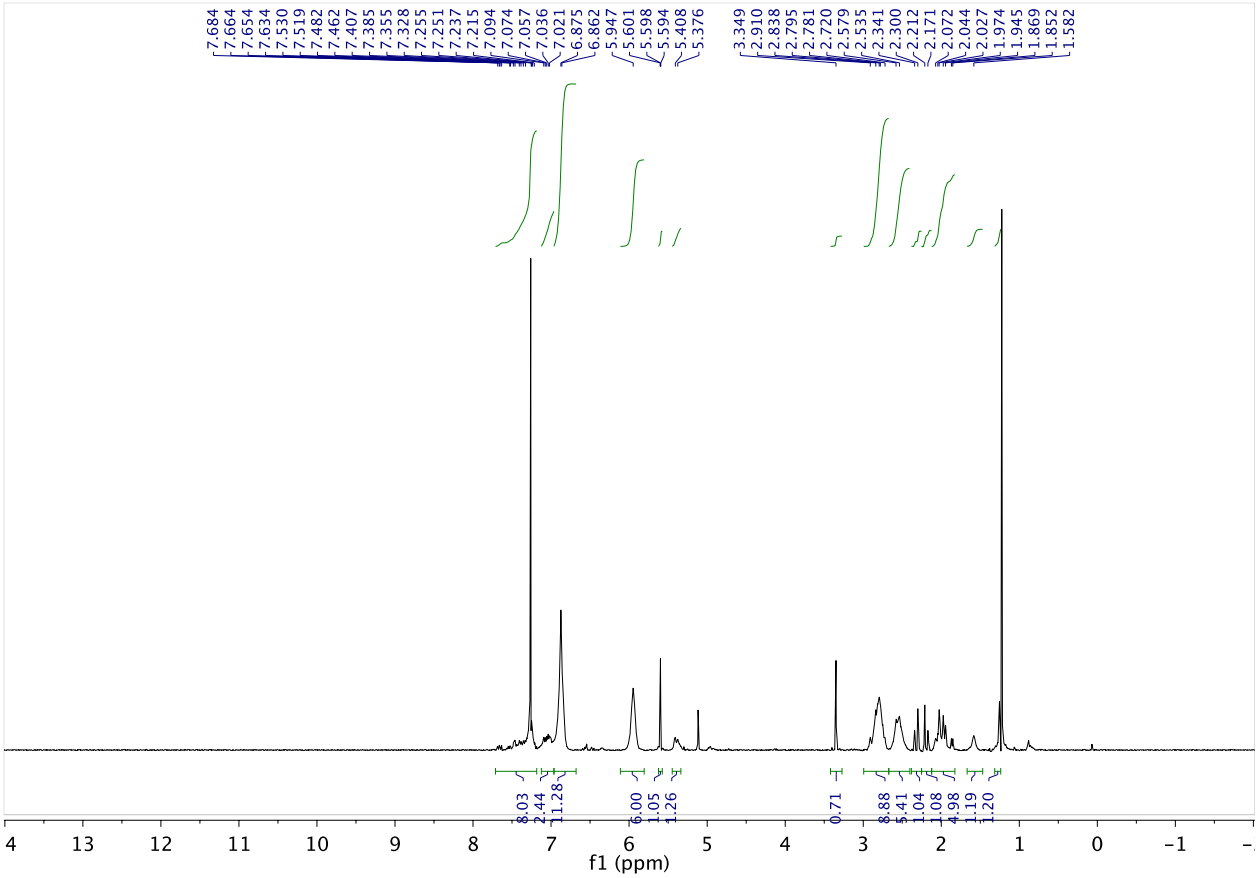
TLC (SiO_2): R_f = 0.30 , 0.37 (CH_2Cl_2 : ethyl acetate = 1:1).

^{1}H NMR: (400 MHz, $CDCl_3$, mixture of isomers): δ = 7.68–7.21 (m, 6H), 7.11-6.97 (m, 2H), 6.95-6.80 (m, 12H), 5.95 (br s, 6H), 5.60 (t, *J* = 1.4 Hz, 1H), 5.44-5.33 (m, 1H), 3.35 (s, 1H), 2.91-2.71 (m, 9H), 2.67-2.43 (m, 5H), 2.32 (d, *J* = 16.5 Hz, 1H) 2.19 (d, *J* = 16.4 Hz, 1H), 2.12 – 1.73 (m, 5H), 1.58 (s, 1H), 1.25 (s, 1H) ppm.

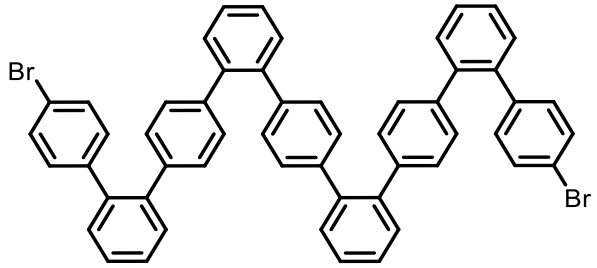
HRMS: (ESI^+) Calculated for $C_{54}H_{52}Br_2O_8$ [M+Na^+] =1009.1921, Found 1009.1928.

FTIR: (neat): 3459, 2900, 1056, 763, 750 cm^{-1}.

*Due to the mixture of stereoisomers, ^{13}C data is not reported.


7.684
7.664
7.654
7.634
7.530
7.519
7.482
7.462
7.407
7.385
7.355
7.328
7.255
7.251
7.237
7.215
7.094
7.074
7.057
7.036
7.021
6.875
6.862
5.947
5.601
5.598
5.594
5.408
5.376
3.349
2.910
2.838
2.795
2.781
2.720
2.579
2.535
2.341
2.300
2.212
2.171
2.072
2.044
2.027
1.974
1.945
1.869
1.852
1.582
8.03
2.44
11.28
6.00
1.05
1.26
0.71
8.88
5.41
1.04
1.08
4.98
1.19
1.20
f1 (ppm)

4,4'''''''''-dibromo-1,1':2',1'':4'',1''':2''',1'''':4'''',1''''':2''''',1'''''':4'''''',1''''''':2''''''',1'''''''':4'''''''',1''''''''-novemphenyl (7.12)



The reaction was conducted in accordance with the general procedure, using **S7.10** (35 mg, 0.035 mmol). The reaction was heated to 85 °C. Flash column chromatography (SiO_2, hexanes:ethyl acetate = 95:5) provided the title compound **7.12** (15 mg, 0.018 mmol) in 51% yield as a colorless solid.

TLC (SiO_2): R_f = 0.60 (hexanes : ethyl acetate = 95:5).

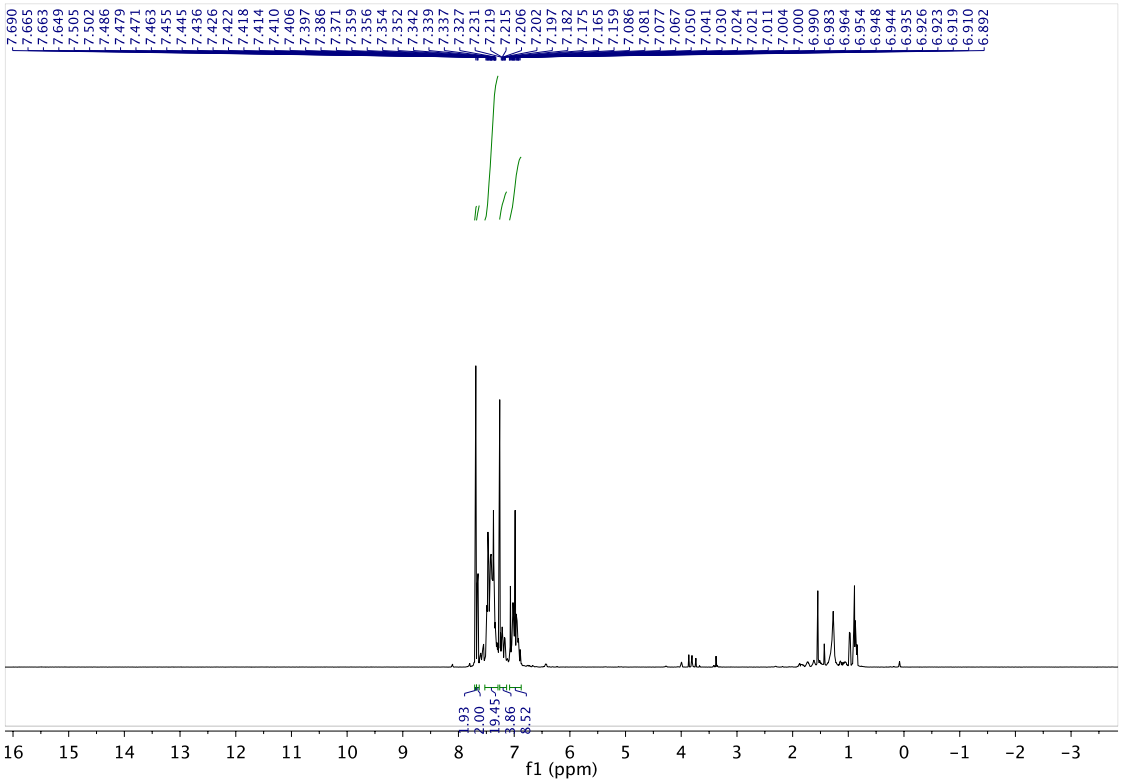
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.69 (s, 2H), 7.66 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.53-7.30 (m, 20H), 7.25-7,15 (m, 4H), 7.09-6.88 (m, 8H) ppm.

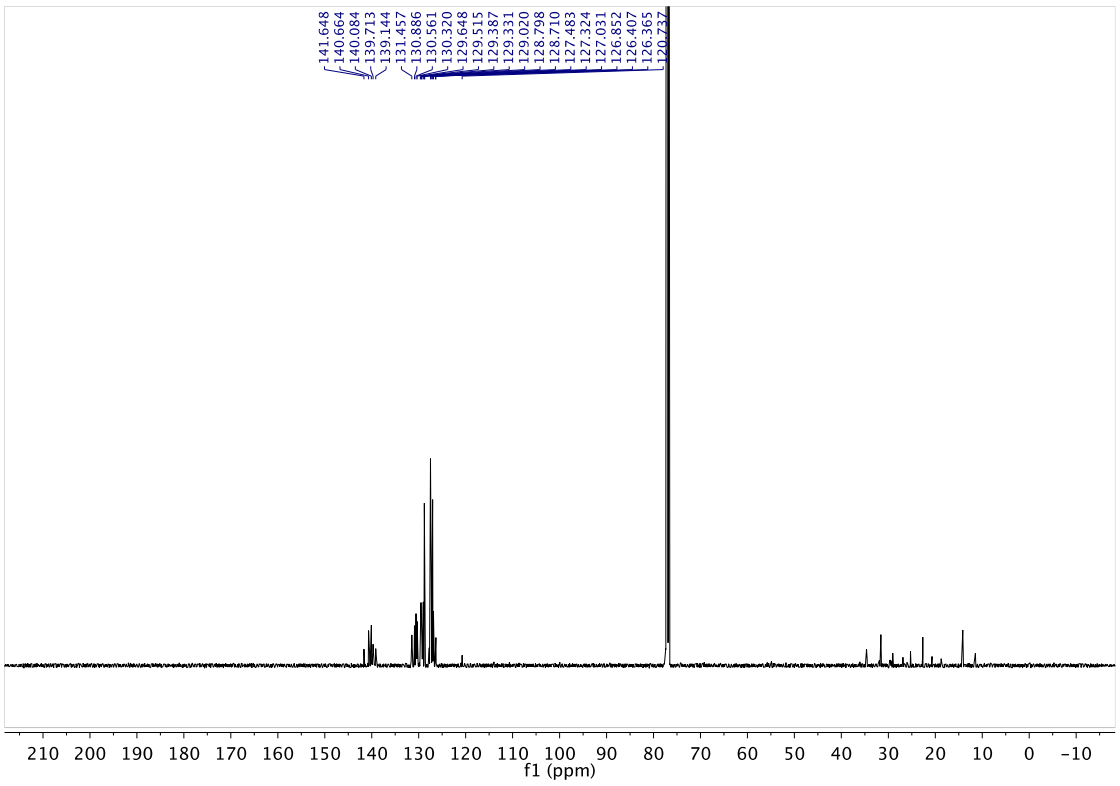
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 141.7, 140.7, 140.1, 139.7, 139.1, 131.5, 130.9, 130.6, 130.3, 129.7, 129.5, 129, 129.4, 129.0, 128.8, 128.7, 127.5, 127.3, 127.0, 126.9, 126.41, 126.37, 120.7 ppm.

HRMS: (CI^+) Calculated for $C_{54}H_{36}$ [M^+] =.842.1184, Found 842.1189.

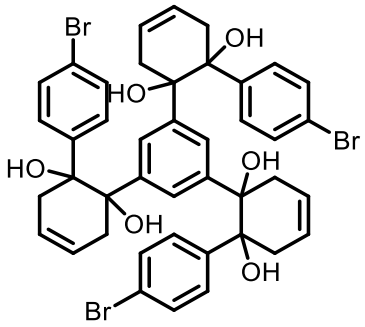
FTIR: (neat): 2985, 1498, 999, 878, 733 cm^{-1}.

MP: >250 °C.


7.690
7.665
7.663
7.649
7.505
7.502
7.486
7.479
7.471
7.463
7.455
7.445
7.436
7.426
7.422
7.418
7.414
7.410
7.406
7.397
7.386
7.371
7.359
7.356
7.354
7.352
7.342
7.339
7.337
7.327
7.231
7.219
7.215
7.206
7.202
7.197
7.182
7.175
7.165
7.159
7.086
7.081
7.077
7.067
7.050
7.041
7.030
7.024
7.021
7.011
7.004
7.000
6.990
6.983
6.964
6.954
6.948
6.944
6.935
6.926
6.923
6.919
6.910
6.892
1.93
2.00
19.45
3.86
8.52
f1 (ppm)


141.648
140.664
140.084
139.713
139.144
131.457
130.886
130.561
130.320
129.648
129.515
129.387
129.331
129.020
128.798
128.710
127.483
127.324
127.031
126.852
126.407
126.365
120.732
f1 (ppm)

Cycloadduct S7.11



The reaction was conducted with tris diol **7.9** at 140 ˚C in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:ethyl acetate =80:30 to 45:55) provided the title compound **S7.11** (142.5 mg, 0.16 mmol) in 81% yield as a white solid.

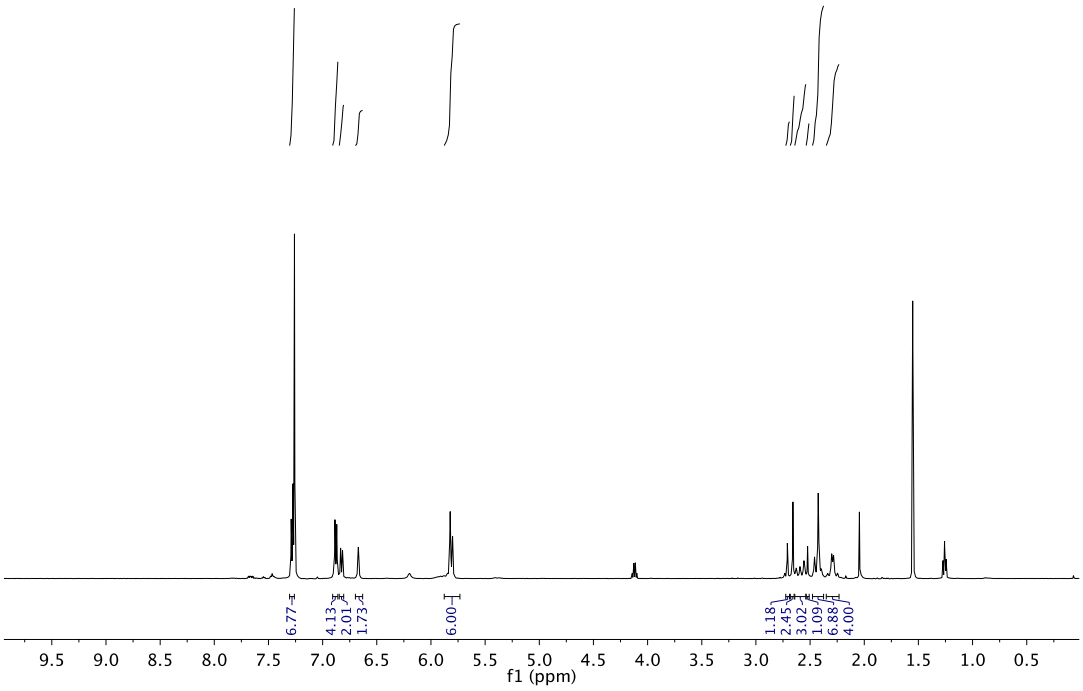
TLC (SiO_2): R_f = 0.20 (hexanes : ethyl acetate = 50:50).

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.2 Hz, 7H), 6.89–6.82 (m, 6H), 6.67 (s, 2H), 2.71–2.28 (m, 18H) ppm.

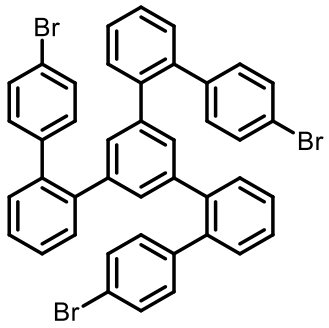
MP: decomposed at ~ 180 ˚C.

HRMS: (ESI) Calculated for $C_{42}H_{39}Br_3O_6$ [M+Na^+] = 903.0157, Found 903.0168.

FTIR: (neat): 1738, 1365, 1217 cm^{-1}.


6.77
4.13
2.01
1.73
6.00
1.18
2.45
3.02
1.09
6.88
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

4,4''''-dibromo-5''-(4'-bromo-[1,1'-biphenyl]-2-yl)-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (7.13)



The reaction was conducted with cycloadduct **S7.11** in accordance with the general procedure. Flash column chromatography (SiO_2, hexanes:DCM = 90:10) provided the title compound **7.13** (138.9 mg, 0.18 mmol) in 90% yield as a white solid.

TLC (SiO_2): R_f = 0.28 (hexanes : DCM = 90:10).

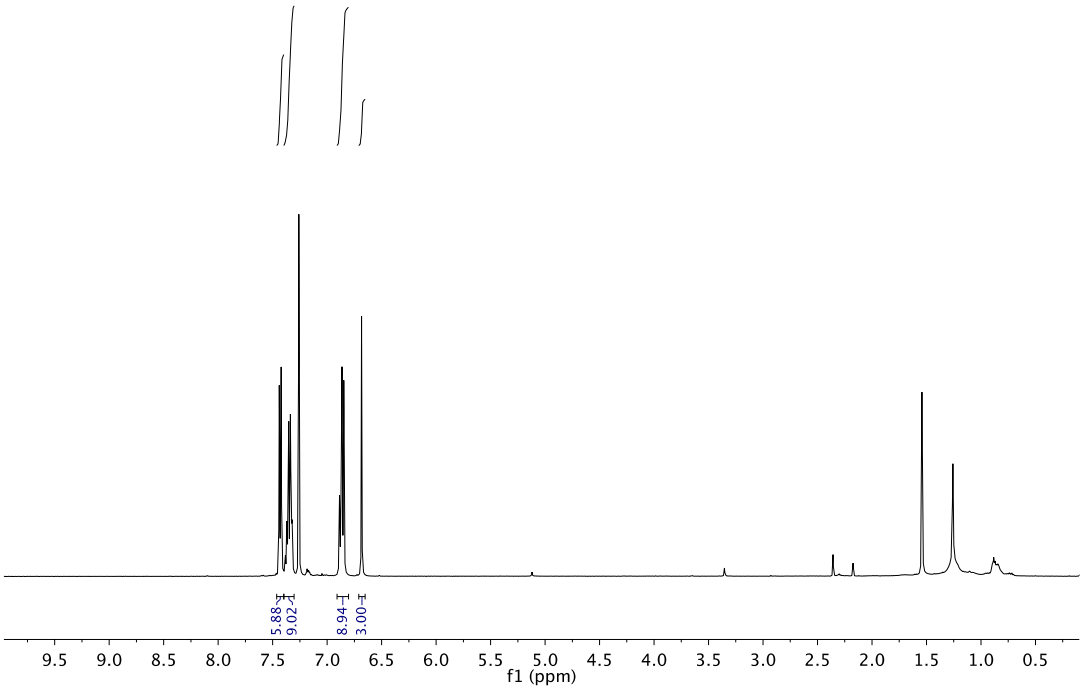
^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 6H), 7.36–7.32 (m, 9H), 6.89–6.85 (m, 9H), 6.68 (s, 3H) ppm.

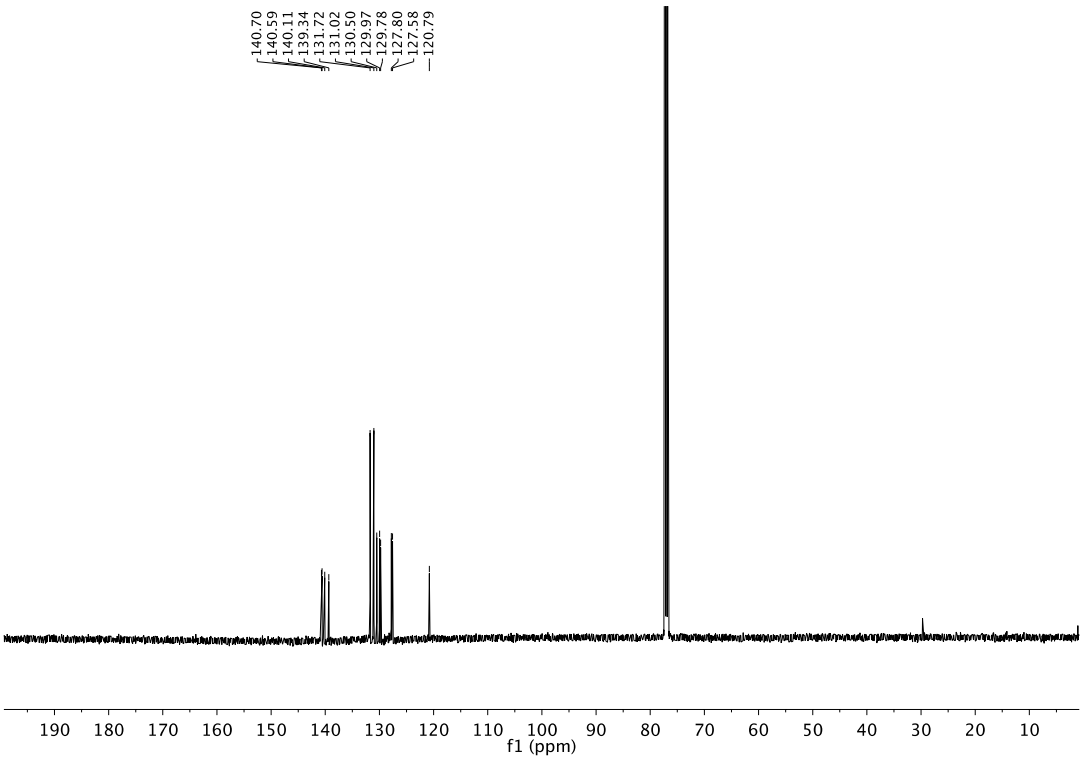
^{13}C NMR: (100 MHz, $CDCl_3$): δ = 140.7. 140.6, 140.1, 139.3, 131.7, 131.0, 130.5, 130.0, 129.8, 127.8, 127.6, 120.8 ppm.

MP: >250°C.

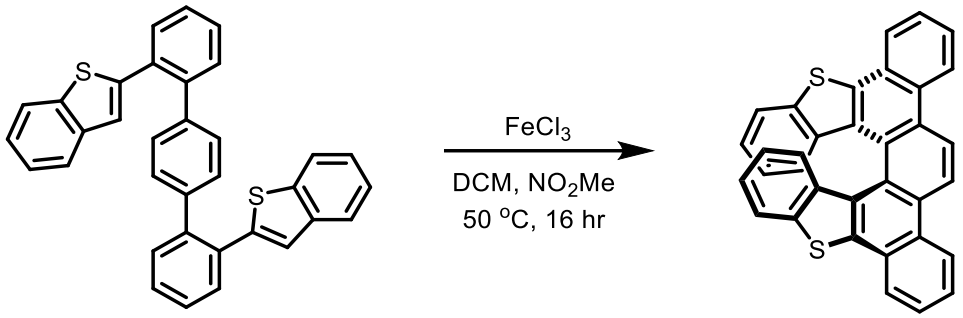
HRMS: (CI^+) Calculated for $C_{42}H_{27}Br_3$ [M^+] = 769.9642, Found 769.9670.

FTIR: (neat): 2362, 2342, 1739, 1366, 1217 cm^{-1}.


5.88
9.02
8.94
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


140.70
140.59
140.11
139.34
131.72
131.02
130.50
129.97
129.78
127.80
127.58
120.79
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Synthesis of Helical Compound (7.14)



7.10c **7.14**

To a resealable pressure tube (c.a. 13×1000) was added **7.10c** (37.1 mg, 0.075 mmol, 100 mol%). Dichloromethane (3 mL) was added followed by $FeCl_3$ (121.7 mg, 0.75 mmol, 1000 mol%) in nitromethane (3 mL). The tube was placed in 50 °C oil bath. When judged complete by TLC (16 h), the tube was removed from the oil bath and allowed to cool to room temperature. Then methanol (3 mL) was added to the reaction mixture. The volatiles were removed in vacuo, and the residue was subjected to flash column chromatography (SiO_2: hexanes/DCM = 4:1) to provide the title compound **7.14** (20.2 mg, 0.041 mmol) as a white solid in 55% yield.

TLC (SiO_2): R_f = 0.79 (hexanes : DCM = 4:1).

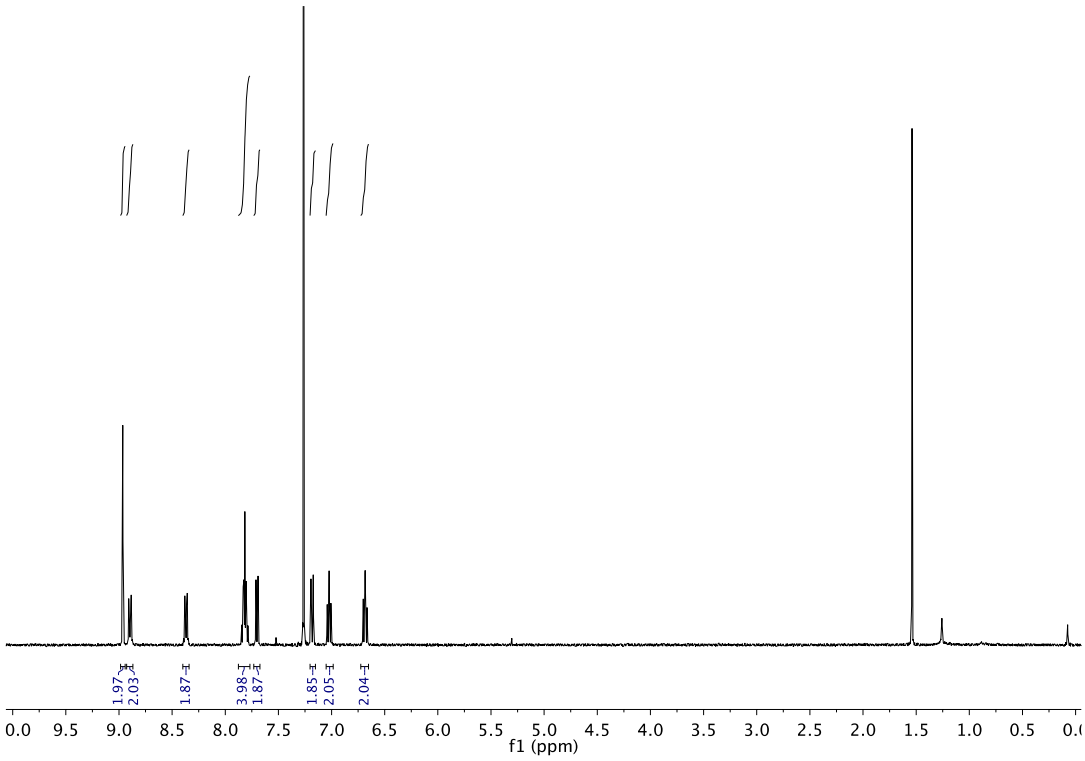
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.96 (s, 2H), 8.91 - 8.82 (m, 2H), 8.38 - 8.36 (m, 2H), 7.85 - 7.78 (m, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 7.02 (dd, J = 8.6, 7.2 Hz, 2H), 6.68 (dd, J = 8.6, 7.2 Hz, 2H) ppm.

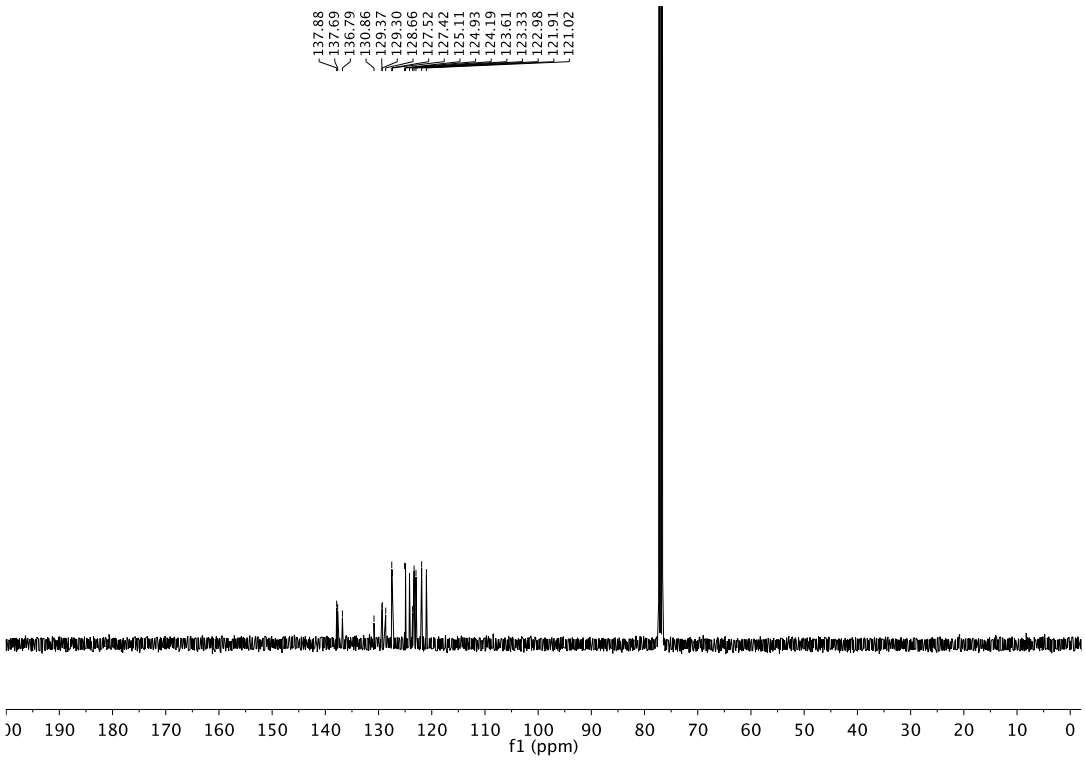
^{13}C NMR: δ 137.9, 137.7, 136.8, 130.9, 129.4, 129.3, 128.7, 127.5, 127.4, 125.1, 124.9, 124.2, 123.6, 123.4, 123.0, 121.9, 121.0 ppm.

MP: 354 °C (sublimed)

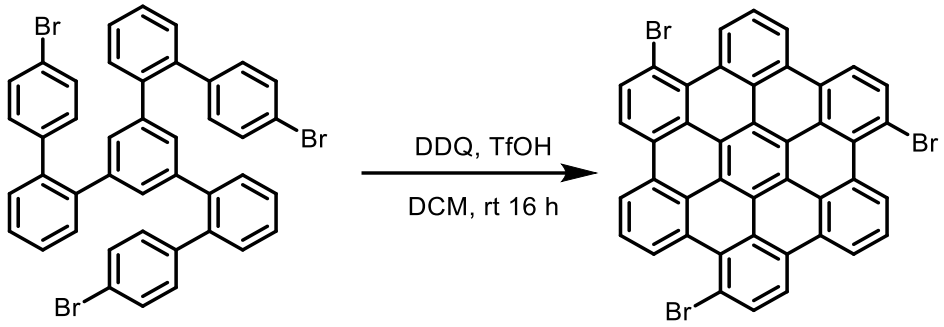
HRMS: (ESI) Calculated for $C_{34}H_{18}S_2$ [M^+] = 490.0850, Found 490.0849.

FTIR: (neat) 3056, 2925, 2852, 1472, 1446, 1261, 1071, 1025, 936, 762, 748, 730 cm^{-1}


1.97
2.03
1.87
3.98
1.87
1.85
2.05
2.04
f1 (ppm)


137.88
137.69
136.79
130.86
129.37
129.30
128.66
127.52
127.42
125.11
124.93
124.19
123.61
123.33
122.98
121.91
121.02
f1 (ppm)

Synthesis of Carbon Nanodot (7.15)



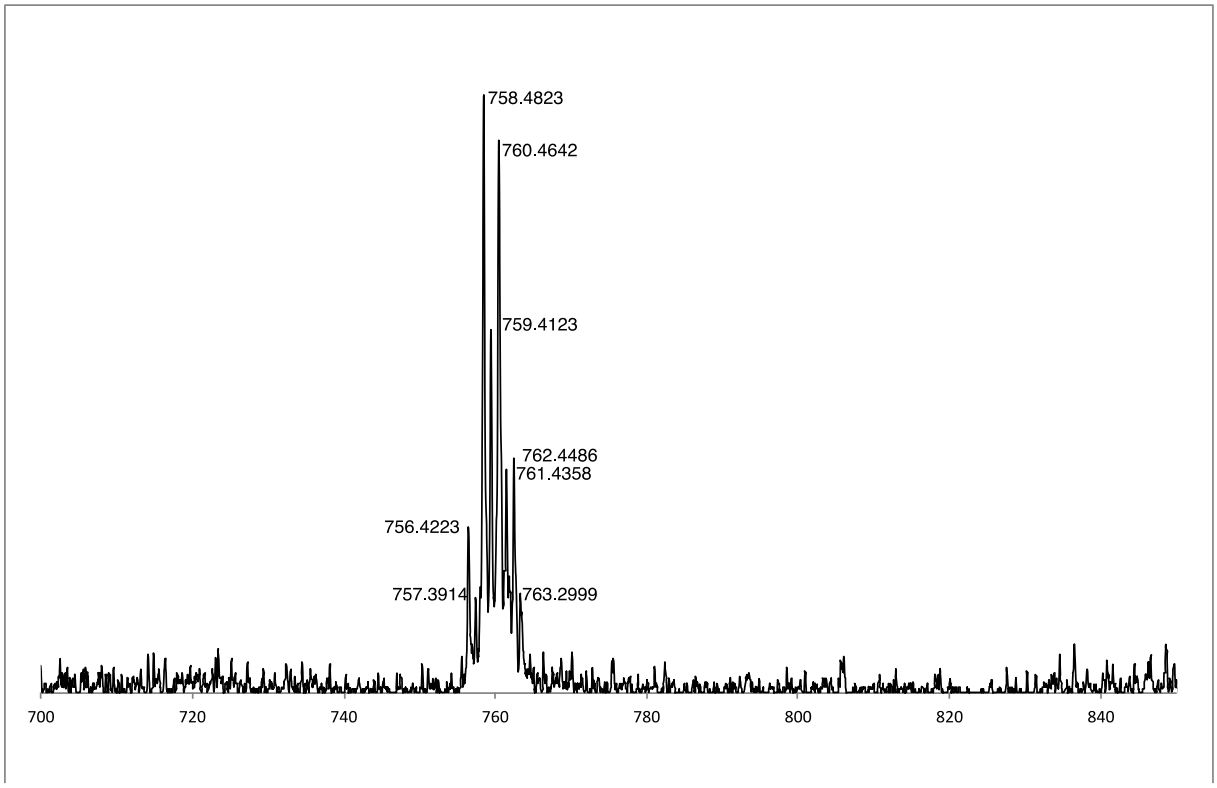
7.13 **7.15**

To a resealable pressure tube (c.a. 13×1000) was added **7.13** (77.1 mg, 0.10 mmol, 100 mol%) and DDQ (136.2 mg, 0.60 mmol, 600 mol%). Dichloromethane (7.7 mL) was added followed by TfOH (53 μL, 0.60 mmol, 600 mol%). The tube was stirred at ambient temperature. After 16 h, MeOH (7.7 mL) was added followed by water (7.7 mL). The yellow precipitation was separated by filtration and washed by DCM, THF, water, and MeOH. The residue was dried under reduced pressure to provide the title compound **7.15** (56.1 mg, 0.074 mmol) as a dark yellow solid in 74% yield.

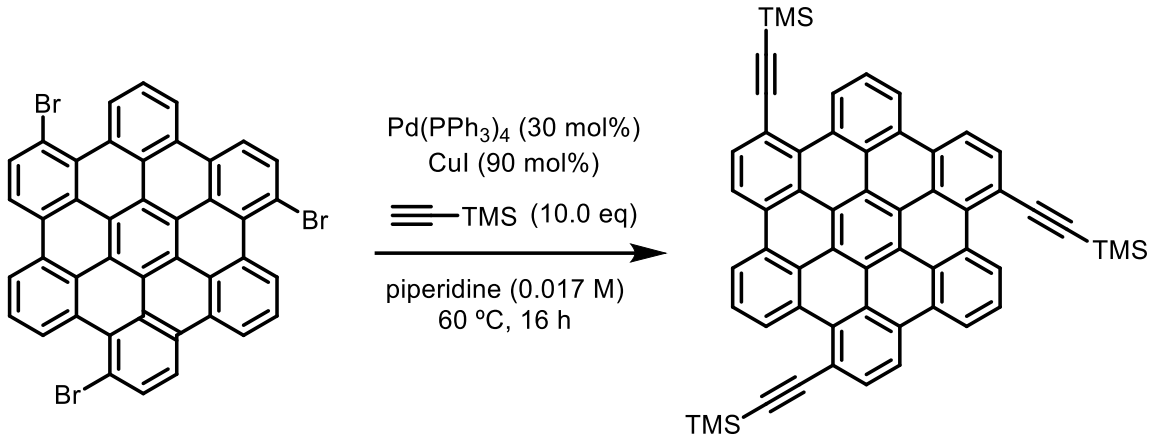
MP: >250 °C.

MALDI-TOF: (TCNQ as a matrix) Calculated for $C_{42}H_{15}Br_3$ [M^+] = 755.9, Found 755.9.

FTIR: (neat) 1626, 1370, 831 cm^{-1}


758.4823
760.4642
759.4123
762.4486
761.4358
756.4223
757.3914
763.2999
700
720
740
760
780
800
820
840

Synthesis of Carbon Nanodot (7.15)



7.15 **7.16**

To a resealable pressure tube (c.a. 13×1000) was added $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%), CuI (1.9 mg, 0.001 mmol, 10 mol%), and **7.15** (75.9 mg, 0.10 mmol, 100 mol). Freshly distilled piperidine (5.9 mL) was added to the tube followed by trimethylsilylacetylene (0.14 mL, 1.0 mmol, 10 eq). The tube was placed in 60 °C oil bath. After 16 h, MeOH (20 mL) was added followed by water (10 mL). The yellow precipitation was separated by filtration and washed by MeOH and water repeatedly. The residue was subjected to flash column chromatography (SiO_2; hexanes:DCM = 5:95 to 20:80) to furnish the title compound **7.16** (34.0 mg, 0.042 mmol) in 42% yield as a bright yellow solid.

TLC (SiO_2): R_f = 0.25 (hexanes : DCM = 80:20).

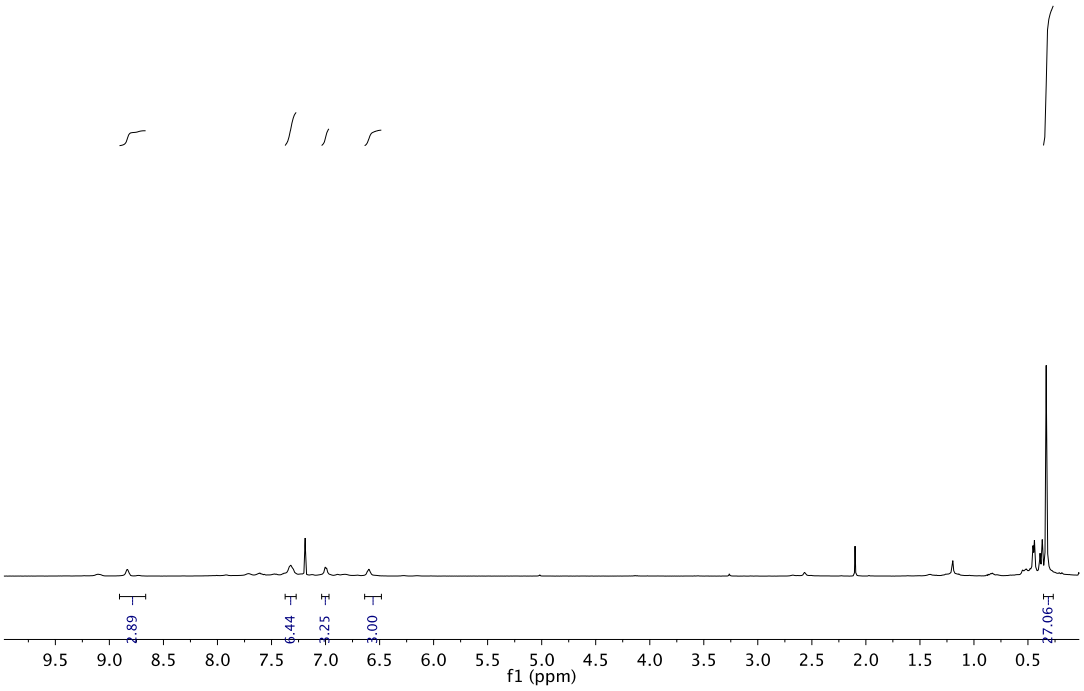
^{1}H NMR: (400 MHz, $CDCl_3/CS_2$ = 1:1): δ = 8.83 (d, *J* = 6.8 Hz, 3H), 7.34–7.30 (m, 6H), 6.99 (d, *J* = 7.1 Hz, 3H), 6.60 (t, *J* = 6.8 Hz, 3H), 0.33 (s, 27H) ppm.

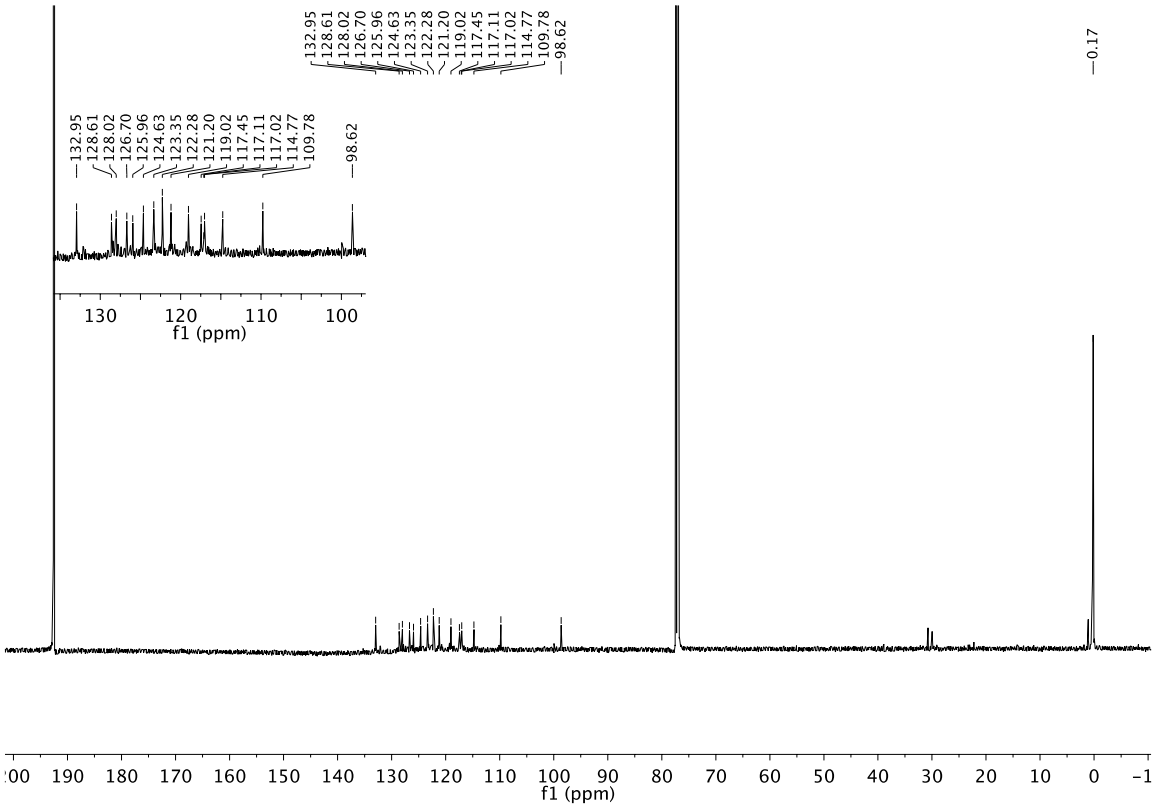
^{13}C NMR: (100 MHz, $CDCl_3/CS_2$ = 1:1): δ = 133.0, 128.6, 128.0, 126.7, 126.0, 124.6, 123.4, 122.3, 121.2, 119.0, 117.5, 117.1, 117.0, 114.8, 109.8, 98.6, 0.17 ppm.

MP: >250 °C.

HRMS: (CI^+) Calculated for $C_{57}H_{42}Si_3$ $[M+H^+]$ =811.2667, Found 811.2667.

FTIR: (neat): 2362, 1738, 1365, 1216, 840 cm^{-1}.


2.89
6.44
3.25
3.00
27.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


132.95
128.61
128.02
126.70
125.96
124.63
123.35
122.28
121.20
119.02
117.45
117.11
117.02
114.77
109.78
98.62
0.17
130 120 110 100
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Single Crystal Diffraction Data

X-ray Experimental for complex **7.11**:

X-ray Experimental for $C_{42}H_{28}Br_2$: Crystals grew as clusters of colorless prisms by slow evaporation from DCM and pentanes. The data crystal was cut from cluster of crystals and had approximate dimensions; 0.34 x 0.23 x 0.20 mm. The data were collected at room temperature on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1323 frames of data were collected using ω and ϕ-scans with a scan range of 0.8° and a counting time of 44 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.[34] The structure was solved by direct methods using Superflip[35] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[36] Structure analysis was aided by use of the programs PLATON98[37] and WinGX.[38] The hydrogen atoms bound to carbon atoms were calculated in idealized positions with Uiso set to 1.2xUeq of the attached carbon atom.

The function, Σw(|Fo|2 - |Fc|2)2, was minimized, where w = 1/[(□(Fo))2 + (0.0785*P)2 + (2.1969*P)] and P = (|Fo|2 + 2|Fc|2)/3. Rw(F2) refined to 0.182, with R(F) equal to 0.0647 and a goodness of fit, S, = 1.04. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[39] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[40] All figures were generated using SHELXTL/PC.[82] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 7.2. Crystal data and structure refinement for **7.11**.

Empirical formula	C42 H28 Br2	
Formula weight	692.46	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.928(2) Å	□= 91.365(8)°.
	b = 11.964(3) Å	□= 90.705(8)°.
	c = 13.330(4) Å	□ = 93.476(6)°.
Volume	1579.7(7) $Å^3$	
Z	2	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	2.596 mm^{-1}	
F(000)	700	
Crystal size	0.34 x 0.23 x 0.20 mm^3	
Theta range for data collection	1.528 to 25.387°.	
Index ranges	-8<=h<=11, -14<=k<=14, -15<=l<=16	
Reflections collected	30260	
Independent reflections	5777 [R(int) = 0.0750]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.862	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5777 / 0 / 397	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1562	
R indices (all data)	R1 = 0.1287, wR2 = 0.1819	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.725 and -1.270 e.$Å^{-3}$	

Table 7.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7.11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	-1314(6)	5691(5)	2952(5)	56(2)
C2	-2451(6)	6149(5)	2617(5)	57(2)
C3	-2614(5)	7278(5)	2823(4)	46(1)
C4	-1647(5)	7937(4)	3359(4)	39(1)
C5	-514(6)	7427(5)	3715(5)	52(2)
C6	-357(6)	6305(6)	3518(5)	63(2)
C7	-1847(5)	9134(4)	3574(4)	39(1)
C8	-3100(5)	9431(5)	3946(4)	45(1)
C9	-3323(6)	10532(5)	4204(4)	54(2)
C10	-2315(6)	11354(5)	4095(5)	57(2)
C11	-1094(6)	11088(5)	3713(5)	53(2)
C12	-843(5)	9987(4)	3444(4)	40(1)
C13	499(5)	9788(4)	3000(4)	34(1)
C14	629(5)	9287(4)	2060(4)	37(1)
C15	1881(5)	9187(4)	1637(4)	36(1)
C16	3061(5)	9581(4)	2132(4)	33(1)
C17	2921(5)	10061(4)	3091(4)	42(1)
C18	1681(5)	10172(4)	3507(4)	45(1)
C19	4417(5)	9551(4)	1681(4)	34(1)
C20	5250(6)	10532(5)	1738(4)	48(1)
C21	6514(6)	10605(5)	1321(5)	55(2)
C22	6978(6)	9676(6)	831(5)	55(2)
C23	6186(5)	8706(5)	767(4)	46(1)
C24	4909(5)	8611(4)	1204(4)	35(1)
C25	4163(5)	7489(4)	1129(4)	35(1)
C26	3517(5)	7005(4)	1952(4)	38(1)
C27	2876(5)	5941(4)	1881(4)	39(1)
C28	2858(5)	5324(4)	994(4)	39(1)
C29	3483(6)	5796(5)	173(4)	48(2)
C30	4116(6)	6855(5)	252(4)	48(2)
C31	2100(5)	4182(4)	871(4)	39(1)

C32	1248(6)	4009(5)	40(4)	53(2)
C33	469(6)	3019(5)	-113(5)	62(2)
C34	526(6)	2188(5)	575(5)	59(2)
C35	1381(6)	2334(5)	1401(4)	47(1)
C36	2169(5)	3334(4)	1568(4)	42(1)
C37	3029(5)	3419(4)	2495(4)	39(1)
C38	4413(6)	3651(5)	2471(4)	45(1)
C39	5195(6)	3652(5)	3331(4)	48(2)
C40	4589(6)	3455(5)	4239(4)	47(1)
C41	3226(6)	3242(5)	4291(5)	56(2)
C42	2466(6)	3213(5)	3431(5)	55(2)
Br1	-1063(1)	4160(1)	2606(1)	94(1)
Br2	5656(1)	3510(1)	5435(1)	71(1)

Table **7.4**. Bond lengths [Å] and angles [°] for **7.11**.

C1-C2	1.359(9)	C19-C20	1.394(7)
C1-C6	1.372(9)	C19-C24	1.395(7)
C1-Br1	1.910(6)	C20-C21	1.378(8)
C2-C3	1.392(8)	C20-H20	0.93
C2-H2	0.93	C21-C22	1.381(9)
C3-C4	1.385(7)	C21-H21	0.93
C3-H3	0.93	C22-C23	1.362(8)
C4-C5	1.396(7)	C22-H22	0.93
C4-C7	1.479(7)	C23-C24	1.402(7)
C5-C6	1.381(8)	C23-H23	0.93
C5-H5	0.93	C24-C25	1.494(7)
C6-H6	0.93	C25-C30	1.377(7)
C7-C12	1.398(7)	C25-C26	1.397(7)
C7-C8	1.407(7)	C26-C27	1.389(7)
C8-C9	1.385(8)	C26-H26	0.93
C8-H8	0.93	C27-C28	1.377(7)
C9-C10	1.372(8)	C27-H27	0.93
C9-H9	0.93	C28-C29	1.380(7)
C10-C11	1.373(8)	C28-C31	1.524(7)
C10-H10	0.93	C29-C30	1.380(8)
C11-C12	1.395(7)	C29-H29	0.93
C11-H11	0.93	C30-H30	0.93
C12-C13	1.494(7)	C31-C32	1.389(7)
C13-C14	1.387(7)	C31-C36	1.395(7)
C13-C18	1.394(7)	C32-C33	1.385(8)
C14-C15	1.382(7)	C32-H32	0.93
C14-H14	0.93	C33-C34	1.371(9)
C15-C16	1.389(7)	C33-H33	0.93
C15-H15	0.93	C34-C35	1.383(8)
C16-C17	1.400(7)	C34-H34	0.93
C16-C19	1.484(7)	C35-C36	1.401(7)
C17-C18	1.369(7)	C35-H35	0.93
C17-H17	0.93	C36-C37	1.491(7)
C18-H18	0.93	C37-C38	1.386(7)

C37-C42	1.394(8)	C40-C41	1.364(8)
C38-C39	1.377(7)	C40-Br2	1.900(6)
C38-H38	0.93	C41-C42	1.364(8)
C39-C40	1.377(8)	C41-H41	0.93
C39-H39	0.93	C42-H42	0.93

C2-C1-C6	121.5(6)	C10-C11-C12	121.3(6)
C2-C1-Br1	118.3(5)	C10-C11-H11	119.4
C6-C1-Br1	120.2(5)	C12-C11-H11	119.4
C1-C2-C3	118.8(6)	C11-C12-C7	119.5(5)
C1-C2-H2	120.6	C11-C12-C13	117.3(5)
C3-C2-H2	120.6	C7-C12-C13	123.2(5)
C4-C3-C2	121.5(5)	C14-C13-C18	117.4(5)
C4-C3-H3	119.3	C14-C13-C12	122.5(4)
C2-C3-H3	119.3	C18-C13-C12	120.0(5)
C3-C4-C5	117.9(5)	C15-C14-C13	121.2(5)
C3-C4-C7	120.5(5)	C15-C14-H14	119.4
C5-C4-C7	121.6(5)	C13-C14-H14	119.4
C6-C5-C4	120.6(6)	C14-C15-C16	121.6(5)
C6-C5-H5	119.7	C14-C15-H15	119.2
C4-C5-H5	119.7	C16-C15-H15	119.2
C1-C6-C5	119.6(6)	C15-C16-C17	116.7(5)
C1-C6-H6	120.2	C15-C16-C19	123.3(5)
C5-C6-H6	120.2	C17-C16-C19	119.9(4)
C12-C7-C8	118.1(5)	C18-C17-C16	121.7(5)
C12-C7-C4	123.3(5)	C18-C17-H17	119.1
C8-C7-C4	118.6(5)	C16-C17-H17	119.1
C9-C8-C7	121.1(5)	C17-C18-C13	121.3(5)
C9-C8-H8	119.5	C17-C18-H18	119.4
C7-C8-H8	119.5	C13-C18-H18	119.4
C10-C9-C8	120.0(5)	C20-C19-C24	118.2(5)
C10-C9-H9	120.0	C20-C19-C16	117.4(5)
C8-C9-H9	120.0	C24-C19-C16	124.4(4)
C11-C10-C9	120.0(6)	C21-C20-C19	122.2(6)
C11-C10-H10	120.0	C21-C20-H20	118.9
C9-C10-H10	120.0	C19-C20-H20	118.9

C22-C21-C20	119.1(5)	C33-C32-C31	121.6(6)
C22-C21-H21	120.4	C33-C32-H32	119.2
C20-C21-H21	120.4	C31-C32-H32	119.2
C23-C22-C21	119.9(6)	C34-C33-C32	119.5(6)
C23-C22-H22	120.1	C34-C33-H33	120.3
C21-C22-H22	120.1	C32-C33-H33	120.3
C22-C23-C24	121.8(6)	C33-C34-C35	119.9(6)
C22-C23-H23	119.1	C33-C34-H34	120.0
C24-C23-H23	119.1	C35-C34-H34	120.0
C19-C24-C23	118.8(5)	C34-C35-C36	121.2(5)
C19-C24-C25	124.3(4)	C34-C35-H35	119.4
C23-C24-C25	116.9(5)	C36-C35-H35	119.4
C30-C25-C26	116.2(5)	C31-C36-C35	118.7(5)
C30-C25-C24	121.8(5)	C31-C36-C37	124.3(5)
C26-C25-C24	122.0(5)	C35-C36-C37	117.0(5)
C27-C26-C25	121.3(5)	C38-C37-C42	117.0(5)
C27-C26-H26	119.4	C38-C37-C36	122.5(5)
C25-C26-H26	119.4	C42-C37-C36	120.5(5)
C28-C27-C26	121.0(5)	C39-C38-C37	121.3(5)
C28-C27-H27	119.5	C39-C38-H38	119.4
C26-C27-H27	119.5	C37-C38-H38	119.4
C27-C28-C29	118.3(5)	C40-C39-C38	119.5(5)
C27-C28-C31	122.5(5)	C40-C39-H39	120.2
C29-C28-C31	119.1(5)	C38-C39-H39	120.2
C28-C29-C30	120.2(5)	C41-C40-C39	120.7(5)
C28-C29-H29	119.9	C41-C40-Br2	119.6(4)
C30-C29-H29	119.9	C39-C40-Br2	119.7(4)
C25-C30-C29	123.0(5)	C40-C41-C42	119.3(6)
C25-C30-H30	118.5	C40-C41-H41	120.4
C29-C30-H30	118.5	C42-C41-H41	120.4
C32-C31-C36	119.0(5)	C41-C42-C37	122.2(5)
C32-C31-C28	117.3(5)	C41-C42-H42	118.9
C36-C31-C28	123.6(5)	C37-C42-H42	118.9

Table 7.5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7.11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	53(4)	40(3)	77(5)	6(3)	27(4)	6(3)
C2	53(4)	50(4)	68(4)	-2(3)	6(3)	-2(3)
C3	41(3)	52(4)	46(3)	9(3)	1(3)	7(3)
C4	38(3)	42(3)	37(3)	8(3)	5(2)	2(3)
C5	42(3)	48(4)	67(4)	15(3)	1(3)	-2(3)
C6	40(3)	61(5)	90(5)	24(4)	13(3)	8(3)
C7	40(3)	43(3)	35(3)	8(2)	3(2)	6(3)
C8	38(3)	51(4)	46(3)	6(3)	2(3)	0(3)
C9	41(3)	69(5)	52(4)	-5(3)	8(3)	17(3)
C10	66(4)	45(4)	62(4)	-2(3)	7(3)	11(3)
C11	49(4)	46(4)	64(4)	-4(3)	11(3)	2(3)
C12	38(3)	41(3)	40(3)	2(3)	1(2)	3(3)
C13	38(3)	27(3)	37(3)	2(2)	4(2)	2(2)
C14	36(3)	34(3)	41(3)	3(2)	-4(2)	0(2)
C15	42(3)	32(3)	33(3)	-2(2)	-1(2)	0(2)
C16	36(3)	24(3)	38(3)	5(2)	-1(2)	1(2)
C17	35(3)	45(3)	44(3)	-5(3)	-6(3)	-1(2)
C18	50(4)	47(4)	37(3)	-6(3)	-7(3)	0(3)
C19	35(3)	35(3)	33(3)	9(2)	-1(2)	-1(2)
C20	47(4)	45(4)	49(4)	5(3)	0(3)	0(3)
C21	49(4)	50(4)	65(4)	13(3)	-3(3)	-11(3)
C22	39(3)	67(5)	60(4)	26(3)	6(3)	0(3)
C23	44(3)	45(4)	50(4)	11(3)	6(3)	8(3)
C24	36(3)	38(3)	33(3)	11(2)	2(2)	3(2)
C25	38(3)	32(3)	36(3)	3(2)	3(2)	8(2)
C26	50(3)	34(3)	31(3)	2(2)	3(2)	6(3)
C27	51(3)	36(3)	30(3)	8(2)	11(2)	4(3)
C28	49(3)	35(3)	36(3)	5(3)	3(3)	8(2)
C29	74(4)	36(3)	35(3)	-3(3)	15(3)	4(3)
C30	66(4)	42(4)	36(3)	10(3)	20(3)	6(3)
C31	49(3)	33(3)	35(3)	-2(2)	7(3)	4(2)

C32	65(4)	47(4)	46(4)	-1(3)	-2(3)	9(3)
C33	68(4)	57(4)	59(4)	-13(4)	-19(3)	5(3)
C34	60(4)	43(4)	71(5)	-10(3)	-2(3)	-5(3)
C35	58(4)	33(3)	49(4)	4(3)	9(3)	1(3)
C36	46(3)	37(3)	44(3)	-5(3)	5(3)	5(3)
C37	47(3)	23(3)	46(3)	5(2)	3(3)	0(2)
C38	52(4)	48(3)	36(3)	1(3)	16(3)	4(3)
C39	45(3)	52(4)	48(4)	2(3)	1(3)	4(3)
C40	63(4)	37(3)	42(4)	3(3)	0(3)	12(3)
C41	58(4)	67(4)	43(4)	16(3)	9(3)	-2(3)
C42	47(4)	63(4)	54(4)	12(3)	8(3)	-5(3)
Br1	81(1)	52(1)	151(1)	2(1)	32(1)	15(1)
Br2	84(1)	76(1)	54(1)	-4(1)	-15(1)	18(1)

Table 7.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **7.11**.

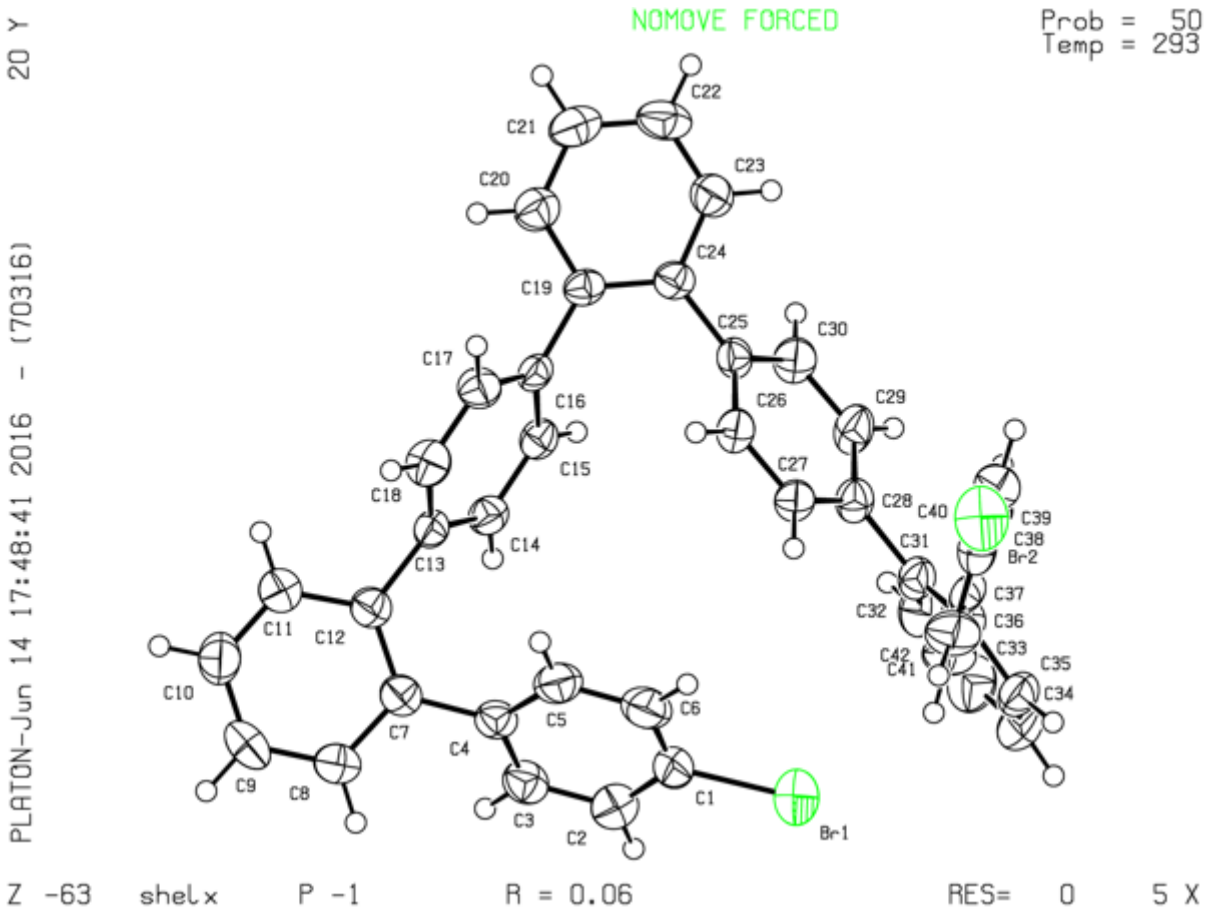
	x	y	z	U(eq)
H2	-3108	5715	2256	69
H3	-3389	7597	2596	55
H5	142	7847	4089	63
H6	392	5967	3768	76
H8	-3790	8879	4019	54
H9	-4156	10714	4452	64
H10	-2460	12092	4279	69
H11	-420	11653	3633	63
H14	-141	9014	1708	45
H15	1935	8847	1005	43
H17	3691	10310	3455	50
H18	1625	10510	4139	54
H20	4942	11158	2069	57
H21	7047	11271	1367	66
H22	7829	9713	547	66
H23	6501	8091	423	55
H26	3517	7403	2560	46
H27	2452	5640	2440	47
H29	3478	5399	-435	58
H30	4529	7153	-312	57
H32	1200	4573	-425	63
H33	-88	2918	-678	74
H34	-10	1528	486	70
H35	1434	1758	1853	56
H38	4822	3809	1862	54
H39	6126	3785	3300	58
H41	2820	3118	4907	67
H42	1541	3049	3469	66

Table 7.7. Torsion angles [°] for **7.11**.

C6-C1-C2-C3	2.6(9)	C15-C16-C17-C18	-2.3(8)
Br1-C1-C2-C3	-177.0(4)	C19-C16-C17-C18	175.7(5)
C1-C2-C3-C4	0.0(9)	C16-C17-C18-C13	1.5(8)
C2-C3-C4-C5	-1.8(8)	C14-C13-C18-C17	0.1(8)
C2-C3-C4-C7	-179.7(5)	C12-C13-C18-C17	-176.0(5)
C3-C4-C5-C6	1.3(8)	C15-C16-C19-C20	131.3(5)
C7-C4-C5-C6	179.0(5)	C17-C16-C19-C20	-46.4(7)
C2-C1-C6-C5	-3.2(10)	C15-C16-C19-C24	-48.5(7)
Br1-C1-C6-C5	176.4(5)	C17-C16-C19-C24	133.8(5)
C4-C5-C6-C1	1.2(9)	C24-C19-C20-C21	1.6(8)
C3-C4-C7-C12	-134.1(5)	C16-C19-C20-C21	-178.2(5)
C5-C4-C7-C12	48.2(8)	C19-C20-C21-C22	-0.2(9)
C3-C4-C7-C8	47.1(7)	C20-C21-C22-C23	0.1(9)
C5-C4-C7-C8	-130.6(6)	C21-C22-C23-C24	-1.4(9)
C12-C7-C8-C9	-1.9(8)	C20-C19-C24-C23	-2.8(7)
C4-C7-C8-C9	177.0(5)	C16-C19-C24-C23	177.0(5)
C7-C8-C9-C10	0.3(8)	C20-C19-C24-C25	176.9(5)
C8-C9-C10-C11	1.1(9)	C16-C19-C24-C25	-3.3(8)
C9-C10-C11-C12	-0.9(9)	C22-C23-C24-C19	2.8(8)
C10-C11-C12-C7	-0.8(8)	C22-C23-C24-C25	-177.0(5)
C10-C11-C12-C13	177.8(5)	C19-C24-C25-C30	137.0(5)
C8-C7-C12-C11	2.1(7)	C23-C24-C25-C30	-43.3(7)
C4-C7-C12-C11	-176.7(5)	C19-C24-C25-C26	-45.5(7)
C8-C7-C12-C13	-176.3(5)	C23-C24-C25-C26	134.2(5)
C4-C7-C12-C13	4.8(8)	C30-C25-C26-C27	0.4(7)
C11-C12-C13-C14	-122.3(6)	C24-C25-C26-C27	-177.3(5)
C7-C12-C13-C14	56.2(7)	C25-C26-C27-C28	0.2(8)
C11-C12-C13-C18	53.7(7)	C26-C27-C28-C29	-0.7(8)
C7-C12-C13-C18	-127.9(6)	C26-C27-C28-C31	-176.6(5)
C18-C13-C14-C15	-0.8(7)	C27-C28-C29-C30	0.6(8)
C12-C13-C14-C15	175.2(5)	C31-C28-C29-C30	176.6(5)
C13-C14-C15-C16	0.0(8)	C26-C25-C30-C29	-0.5(8)
C14-C15-C16-C17	1.5(7)	C24-C25-C30-C29	177.2(5)
C14-C15-C16-C19	-176.3(4)	C28-C29-C30-C25	0.0(9)

C27-C28-C31-C32	130.4(6)	C31-C36-C37-C38	-56.7(8)
C29-C28-C31-C32	-45.5(7)	C35-C36-C37-C38	123.7(6)
C27-C28-C31-C36	-46.5(8)	C31-C36-C37-C42	126.4(6)
C29-C28-C31-C36	137.7(6)	C35-C36-C37-C42	-53.2(7)
C36-C31-C32-C33	0.0(9)	C42-C37-C38-C39	1.4(8)
C28-C31-C32-C33	-177.0(5)	C36-C37-C38-C39	-175.7(5)
C31-C32-C33-C34	0.6(10)	C37-C38-C39-C40	-2.1(8)
C32-C33-C34-C35	-1.5(10)	C38-C39-C40-C41	1.0(9)
C33-C34-C35-C36	1.9(9)	C38-C39-C40-Br2	-177.7(4)
C32-C31-C36-C35	0.3(8)	C39-C40-C41-C42	0.8(9)
C28-C31-C36-C35	177.1(5)	Br2-C40-C41-C42	179.5(5)
C32-C31-C36-C37	-179.3(5)	C40-C41-C42-C37	-1.5(9)
C28-C31-C36-C37	-2.5(8)	C38-C37-C42-C41	0.5(9)
C34-C35-C36-C31	-1.3(8)	C36-C37-C42-C41	177.6(5)
C34-C35-C36-C37	178.3(5)		

Figure 7.1. View of molecule **7.11** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for complex **7.14**:

X-ray Experimental for 3 $C_{34}H_{18}S_2$ – CH_2Cl_2: Crystals grew as long colorless needles by slow evaporation from dichloromethane and pentanes. The data crystal was cut from a larger crystal and had approximate dimensions; 0.52 x 0.14 x 0.11 mm. The data were collected at -173 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 1155 frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 66 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.[34] The structure was solved by direct methods using SIR97[42] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.[36] Structure analysis was aided by use of the programs PLATON98[37] and WinGX.[38]

A molecule of dichloromethane badly disordered around a crystallographic inversion center. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to the solvent molecule were removed by use of the utility SQUEEZE[39] in PLATON98. The function, Σw(|Fo|2 - |Fc|2)2, was minimized, where w = 1/[(σ(Fo))2 + (0.0712*P)2] and P = (|Fo|2 + 2|Fc|2)/3. Rw(F2) refined to 0.183, with R(F) equal to 0.0724 and a goodness of fit, S, = 0.963. Definitions used for calculating R(F), Rw(F2) and the goodness of fit, S, are given below.[40] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[41] All figures were generated using

SHELXTL/PC.9 Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 7.8. Crystal data and structure refinement for **7.14**.

Empirical formula	C103 H56 Cl2 S6	
Formula weight	1556.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.2129(16) Å	□= 90°.
	b = 21.272(4) Å	□= 91.730(11)°.
	c = 36.423(6) Å	□ = 90°.
Volume	7135(2) Å^3	
Z	4	
Density (calculated)	1.449 Mg/m^3	
Absorption coefficient	0.323 mm^{-1}	
F(000)	3216	
Crystal size	0.52 x 0.14 x 0.12 mm^3	
Theta range for data collection	1.915 to 22.873°.	
Index ranges	-10<=h<=9, -23<=k<=23, -39<=l<=39	
Reflections collected	44139	
Independent reflections	9603 [R(int) = 0.1843]	
Completeness to theta = 22.873°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.749	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9603 / 0 / 973	
Goodness-of-fit on F^2	0.963	
Final R indices [I>2sigma(I)]	R1 = 0.0724, wR2 = 0.1467	
R indices (all data)	R1 = 0.1662, wR2 = 0.1829	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.283 and -0.345 e.Å^{-3}	

Table 7.9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7.14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	4616(7)	1218(3)	5532(2)	28(2)
C2	5003(7)	667(3)	5741(2)	37(2)
C3	5893(7)	701(3)	6061(2)	37(2)
C4	6415(7)	163(3)	6225(2)	41(2)
C5	6035(8)	-427(3)	6073(2)	49(2)
C6	5136(7)	-467(3)	5765(2)	39(2)
C7	4576(7)	82(3)	5592(2)	31(2)
C8	3567(7)	61(3)	5271(2)	32(2)
C9	3026(7)	617(3)	5114(2)	28(2)
C10	3755(7)	1201(3)	5216(2)	31(2)
C11	3840(7)	1797(3)	5010(2)	28(2)
C12	3352(6)	1951(3)	4656(2)	29(2)
C13	3586(7)	2549(3)	4520(2)	42(2)
C14	4323(8)	2992(3)	4736(2)	45(2)
C15	4860(7)	2847(3)	5076(2)	38(2)
C16	4653(7)	2249(3)	5214(2)	35(2)
C17	3175(7)	-517(3)	5112(2)	34(2)
C18	2266(7)	-547(3)	4813(2)	35(2)
C19	1522(7)	1(3)	4680(2)	29(2)
C20	1790(7)	578(3)	4860(2)	27(2)
C21	508(7)	-41(3)	4370(2)	34(2)
C22	256(7)	-594(3)	4166(2)	38(2)
C23	-750(7)	-616(3)	3881(2)	40(2)
C24	-1548(8)	-88(3)	3781(2)	43(2)
C25	-1317(7)	470(3)	3962(2)	36(2)
C26	-317(7)	501(3)	4259(2)	33(2)
C27	-126(7)	1051(3)	4483(2)	32(2)
C28	778(7)	1087(3)	4788(2)	30(2)
C29	412(7)	1640(3)	5010(2)	30(2)
C30	897(7)	1805(3)	5366(2)	35(2)
C31	338(8)	2338(3)	5527(2)	44(2)

C32	-654(8)	2713(3)	5338(2)	46(2)
C33	-1171(8)	2554(3)	4994(2)	47(2)
C34	-640(8)	2011(3)	4836(2)	40(2)
C35	6333(7)	3267(3)	6407(2)	34(2)
C36	6669(7)	2663(3)	6573(2)	35(2)
C37	7647(7)	2239(3)	6426(2)	36(2)
C38	8042(7)	1711(3)	6613(2)	42(2)
C39	7470(7)	1589(3)	6955(2)	41(2)
C40	6502(7)	1999(3)	7110(2)	39(2)
C41	6087(7)	2562(3)	6921(2)	32(2)
C42	5066(7)	2994(3)	7068(2)	31(2)
C43	4598(7)	3532(3)	6862(2)	33(2)
C44	5440(8)	3704(3)	6553(2)	34(2)
C45	5585(7)	4318(3)	6375(2)	36(2)
C46	5062(7)	4912(3)	6469(2)	39(2)
C47	5382(9)	5427(4)	6261(2)	53(2)
C48	6196(9)	5376(4)	5955(2)	57(2)
C49	6788(9)	4803(4)	5858(2)	55(2)
C50	6494(8)	4278(3)	6073(2)	44(2)
C51	4502(7)	2918(3)	7428(2)	35(2)
C52	3603(7)	3349(3)	7570(2)	37(2)
C53	2988(7)	3839(3)	7353(2)	35(2)
C54	3380(7)	3872(3)	6981(2)	33(2)
C55	1968(8)	4291(3)	7498(2)	41(2)
C56	1655(8)	4298(4)	7874(2)	53(2)
C57	707(9)	4736(4)	8010(2)	61(2)
C58	75(9)	5193(4)	7774(3)	65(3)
C59	374(8)	5194(3)	7417(3)	59(2)
C60	1311(8)	4742(3)	7266(3)	50(2)
C61	1524(8)	4682(3)	6881(2)	48(2)
C62	2429(7)	4235(3)	6733(2)	40(2)
C63	2164(8)	4165(3)	6335(2)	43(2)
C64	2673(8)	3727(3)	6085(2)	48(2)
C65	2219(9)	3739(4)	5726(2)	62(2)
C66	1238(11)	4190(5)	5597(3)	75(3)
C67	670(9)	4608(5)	5836(3)	77(3)

C68	1130(8)	4605(3)	6207(2)	50(2)
C69	6402(7)	2993(3)	2594(2)	29(2)
C70	6657(7)	3030(3)	2212(2)	32(2)
C71	7603(7)	3488(3)	2063(2)	32(2)
C72	8017(7)	3443(3)	1706(2)	37(2)
C73	7495(7)	2957(3)	1485(2)	36(2)
C74	6539(7)	2525(3)	1622(2)	35(2)
C75	6092(7)	2539(3)	1987(2)	28(2)
C76	5086(7)	2097(3)	2138(2)	29(2)
C77	4678(7)	2133(3)	2505(2)	28(2)
C78	5533(7)	2534(3)	2745(2)	29(2)
C79	5781(6)	2513(3)	3146(2)	29(2)
C80	5374(7)	2065(3)	3408(2)	34(2)
C81	5762(7)	2154(3)	3770(2)	34(2)
C82	6536(7)	2680(3)	3886(2)	36(2)
C83	7034(7)	3100(3)	3637(2)	36(2)
C84	6657(7)	3011(3)	3273(2)	30(2)
C85	4494(7)	1612(3)	1916(2)	31(2)
C86	3590(7)	1172(3)	2049(2)	31(2)
C87	3042(7)	1222(3)	2405(2)	26(2)
C88	3490(7)	1751(3)	2620(2)	30(2)
C89	2071(7)	748(3)	2548(2)	28(2)
C90	1649(7)	210(3)	2346(2)	33(2)
C91	769(7)	-235(3)	2490(2)	34(2)
C92	271(7)	-175(3)	2844(2)	37(2)
C93	656(7)	353(3)	3053(2)	37(2)
C94	1547(7)	817(3)	2899(2)	31(2)
C95	1791(7)	1412(3)	3087(2)	31(2)
C96	2627(7)	1881(3)	2939(2)	28(2)
C97	2364(7)	2481(3)	3129(2)	29(2)
C98	2753(7)	3096(3)	3037(2)	36(2)
C99	2309(7)	3583(3)	3255(2)	35(2)
C100	1504(7)	3485(3)	3567(2)	40(2)
C101	1055(7)	2880(3)	3653(2)	39(2)
C102	1473(7)	2396(3)	3430(2)	31(2)
S1	5373(2)	1952(1)	5623(1)	40(1)

S2	-1250(2)	1700(1)	4421(1)	39(1)
S3	7253(2)	3540(1)	6026(1)	49(1)
S4	473(2)	5072(1)	6552(1)	65(1)
S5	7304(2)	3470(1)	2915(1)	37(1)
S6	870(2)	1621(1)	3475(1)	36(1)

Table 7.10. Bond lengths [Å] and angles [°] for **7.14**.

C1-C10	1.376(8)	C19-C20	1.410(8)
C1-C2	1.436(8)	C19-C21	1.444(8)
C1-S1	1.738(6)	C20-C28	1.448(8)
C2-C3	1.408(8)	C21-C22	1.407(8)
C2-C7	1.409(9)	C21-C26	1.432(9)
C3-C4	1.370(8)	C22-C23	1.373(8)
C3-H3	0.95	C22-H22	0.95
C4-C5	1.412(9)	C23-C24	1.384(9)
C4-H4	0.95	C23-H23	0.95
C5-C6	1.377(8)	C24-C25	1.373(8)
C5-H5	0.95	C24-H24	0.95
C6-C7	1.416(8)	C25-C26	1.401(8)
C6-H6	0.95	C25-H25	0.95
C7-C8	1.471(8)	C26-C27	1.433(8)
C8-C9	1.400(8)	C27-C28	1.372(8)
C8-C17	1.401(8)	C27-S2	1.737(6)
C9-C20	1.450(8)	C28-C29	1.469(8)
C9-C10	1.455(8)	C29-C34	1.388(8)
C10-C11	1.476(8)	C29-C30	1.405(8)
C11-C12	1.390(8)	C30-C31	1.383(9)
C11-C16	1.417(8)	C30-H30	0.95
C12-C13	1.386(8)	C31-C32	1.382(9)
C12-H12	0.95	C31-H31	0.95
C13-C14	1.391(9)	C32-C33	1.369(9)
C13-H13	0.95	C32-H32	0.95
C14-C15	1.356(8)	C33-C34	1.386(9)
C14-H14	0.95	C33-H33	0.95
C15-C16	1.384(8)	C34-S2	1.729(7)
C15-H15	0.95	C35-C44	1.362(9)
C16-S1	1.732(6)	C35-C36	1.449(9)
C17-C18	1.356(8)	C35-S3	1.747(7)
C17-H17	0.95	C36-C37	1.393(9)
C18-C19	1.429(8)	C36-C41	1.408(9)
C18-H18	0.95	C37-C38	1.357(9)

C37-H37	0.95	C57-H57	0.95
C38-C39	1.390(9)	C58-C59	1.337(10)
C38-H38	0.95	C58-H58	0.95
C39-C40	1.381(9)	C59-C60	1.415(10)
C39-H39	0.95	C59-H59	0.95
C40-C41	1.429(8)	C60-C61	1.428(10)
C40-H40	0.95	C61-C62	1.384(10)
C41-C42	1.431(9)	C61-S4	1.729(7)
C42-C43	1.429(8)	C62-C63	1.470(9)
C42-C51	1.432(8)	C63-C64	1.394(9)
C43-C54	1.412(9)	C63-C68	1.406(9)
C43-C44	1.435(9)	C64-C65	1.359(9)
C44-C45	1.465(9)	C64-H64	0.95
C45-C46	1.399(9)	C65-C66	1.390(11)
C45-C50	1.407(9)	C65-H65	0.95
C46-C47	1.369(9)	C66-C67	1.359(11)
C46-H46	0.95	C66-H66	0.95
C47-C48	1.368(10)	C67-C68	1.404(10)
C47-H47	0.95	C67-H67	0.95
C48-C49	1.386(10)	C68-S4	1.725(8)
C48-H48	0.95	C69-C78	1.386(8)
C49-C50	1.392(9)	C69-C70	1.419(8)
C49-H49	0.95	C69-S5	1.742(6)
C50-S3	1.730(7)	C70-C75	1.417(8)
C51-C52	1.348(8)	C70-C71	1.426(8)
C51-H51	0.95	C71-C72	1.367(8)
C52-C53	1.415(9)	C71-H71	0.95
C52-H52	0.95	C72-C73	1.389(8)
C53-C54	1.416(9)	C72-H72	0.95
C53-C55	1.455(9)	C73-C74	1.376(8)
C54-C62	1.459(9)	C73-H73	0.95
C55-C60	1.404(9)	C74-C75	1.404(8)
C55-C56	1.407(9)	C74-H74	0.95
C56-C57	1.379(10)	C75-C76	1.442(8)
C56-H56	0.95	C76-C77	1.403(8)
C57-C58	1.411(11)	C76-C85	1.409(8)

C77-C88	1.437(8)	C90-C91	1.362(8)
C77-C78	1.439(8)	C90-H90	0.95
C78-C79	1.474(8)	C91-C92	1.386(8)
C79-C84	1.400(8)	C91-H91	0.95
C79-C80	1.407(8)	C92-C93	1.398(8)
C80-C81	1.369(8)	C92-H92	0.95
C80-H80	0.95	C93-C94	1.410(9)
C81-C82	1.385(8)	C93-H93	0.95
C81-H81	0.95	C94-C95	1.452(8)
C82-C83	1.364(8)	C95-C96	1.380(8)
C82-H82	0.95	C95-S6	1.728(7)
C83-C84	1.375(8)	C96-C97	1.475(8)
C83-H83	0.95	C97-C102	1.400(8)
C84-S5	1.746(6)	C97-C98	1.401(8)
C85-C86	1.353(8)	C98-C99	1.375(8)
C85-H85	0.95	C98-H98	0.95
C86-C87	1.409(8)	C99-C100	1.392(9)
C86-H86	0.95	C99-H99	0.95
C87-C88	1.425(8)	C100-C101	1.390(9)
C87-C89	1.455(8)	C100-H100	0.95
C88-C96	1.452(9)	C101-C102	1.374(8)
C89-C94	1.387(8)	C101-H101	0.95
C89-C90	1.410(8)	C102-S6	1.749(6)

C10-C1-C2	123.3(6)	C5-C4-H4	120.3
C10-C1-S1	113.7(5)	C6-C5-C4	120.7(6)
C2-C1-S1	122.6(5)	C6-C5-H5	119.6
C3-C2-C7	120.8(6)	C4-C5-H5	119.6
C3-C2-C1	121.8(6)	C5-C6-C7	120.9(7)
C7-C2-C1	117.1(6)	C5-C6-H6	119.5
C4-C3-C2	120.5(7)	C7-C6-H6	119.5
C4-C3-H3	119.7	C2-C7-C6	117.6(6)
C2-C3-H3	119.7	C2-C7-C8	119.7(6)
C3-C4-C5	119.3(6)	C6-C7-C8	122.7(6)
C3-C4-H4	120.3	C9-C8-C17	119.3(6)

C9-C8-C7	120.4(6)	C19-C20-C9	118.1(6)
C17-C8-C7	120.2(6)	C28-C20-C9	124.1(6)
C8-C9-C20	118.4(6)	C22-C21-C26	116.5(6)
C8-C9-C10	117.5(6)	C22-C21-C19	123.8(6)
C20-C9-C10	124.1(6)	C26-C21-C19	119.7(6)
C1-C10-C9	119.0(6)	C23-C22-C21	121.7(7)
C1-C10-C11	111.4(5)	C23-C22-H22	119.1
C9-C10-C11	129.3(5)	C21-C22-H22	119.1
C12-C11-C16	118.5(6)	C22-C23-C24	120.8(7)
C12-C11-C10	130.8(6)	C22-C23-H23	119.6
C16-C11-C10	110.5(5)	C24-C23-H23	119.6
C13-C12-C11	119.9(6)	C25-C24-C23	120.2(6)
C13-C12-H12	120.0	C25-C24-H24	119.9
C11-C12-H12	120.0	C23-C24-H24	119.9
C12-C13-C14	119.9(6)	C24-C25-C26	120.0(6)
C12-C13-H13	120.1	C24-C25-H25	120.0
C14-C13-H13	120.1	C26-C25-H25	120.0
C15-C14-C13	121.4(6)	C25-C26-C21	120.8(6)
C15-C14-H14	119.3	C25-C26-C27	122.8(6)
C13-C14-H14	119.3	C21-C26-C27	116.2(6)
C14-C15-C16	119.4(6)	C28-C27-C26	124.6(6)
C14-C15-H15	120.3	C28-C27-S2	113.9(5)
C16-C15-H15	120.3	C26-C27-S2	120.9(5)
C15-C16-C11	120.7(6)	C27-C28-C20	118.3(6)
C15-C16-S1	126.5(5)	C27-C28-C29	110.2(6)
C11-C16-S1	112.8(5)	C20-C28-C29	131.1(6)
C18-C17-C8	121.2(6)	C34-C29-C30	118.5(6)
C18-C17-H17	119.4	C34-C29-C28	112.0(6)
C8-C17-H17	119.4	C30-C29-C28	129.4(6)
C17-C18-C19	121.0(6)	C31-C30-C29	118.9(6)
C17-C18-H18	119.5	C31-C30-H30	120.5
C19-C18-H18	119.5	C29-C30-H30	120.5
C20-C19-C18	118.4(6)	C32-C31-C30	120.9(7)
C20-C19-C21	121.1(6)	C32-C31-H31	119.6
C18-C19-C21	120.5(6)	C30-C31-H31	119.6
C19-C20-C28	117.8(6)	C33-C32-C31	121.2(7)

C33-C32-H32	119.4	C35-C44-C45	111.8(7)
C31-C32-H32	119.4	C43-C44-C45	129.3(6)
C32-C33-C34	118.0(6)	C46-C45-C50	117.6(6)
C32-C33-H33	121.0	C46-C45-C44	131.3(7)
C34-C33-H33	121.0	C50-C45-C44	111.0(6)
C33-C34-C29	122.4(6)	C47-C46-C45	120.5(7)
C33-C34-S2	124.9(5)	C47-C46-H46	119.8
C29-C34-S2	112.6(5)	C45-C46-H46	119.8
C44-C35-C36	124.5(6)	C48-C47-C46	121.3(8)
C44-C35-S3	113.4(5)	C48-C47-H47	119.4
C36-C35-S3	121.6(6)	C46-C47-H47	119.4
C37-C36-C41	120.9(6)	C47-C48-C49	120.5(8)
C37-C36-C35	123.2(7)	C47-C48-H48	119.8
C41-C36-C35	115.4(6)	C49-C48-H48	119.8
C38-C37-C36	120.7(7)	C48-C49-C50	118.5(8)
C38-C37-H37	119.7	C48-C49-H49	120.7
C36-C37-H37	119.7	C50-C49-H49	120.7
C37-C38-C39	120.1(7)	C49-C50-C45	121.5(7)
C37-C38-H38	119.9	C49-C50-S3	125.9(7)
C39-C38-H38	119.9	C45-C50-S3	112.5(5)
C40-C39-C38	121.0(7)	C52-C51-C42	121.2(7)
C40-C39-H39	119.5	C52-C51-H51	119.4
C38-C39-H39	119.5	C42-C51-H51	119.4
C39-C40-C41	119.9(7)	C51-C52-C53	121.8(7)
C39-C40-H40	120.0	C51-C52-H52	119.1
C41-C40-H40	120.0	C53-C52-H52	119.1
C36-C41-C40	117.3(6)	C52-C53-C54	117.4(6)
C36-C41-C42	120.9(6)	C52-C53-C55	122.4(7)
C40-C41-C42	121.7(7)	C54-C53-C55	120.2(6)
C43-C42-C41	120.6(6)	C43-C54-C53	119.7(6)
C43-C42-C51	117.2(6)	C43-C54-C62	123.4(7)
C41-C42-C51	122.2(6)	C53-C54-C62	116.9(7)
C54-C43-C42	118.7(7)	C60-C55-C56	118.8(7)
C54-C43-C44	124.2(6)	C60-C55-C53	120.2(7)
C42-C43-C44	117.1(6)	C56-C55-C53	121.0(7)
C35-C44-C43	118.8(6)	C57-C56-C55	120.4(8)

C57-C56-H56	119.8	C67-C68-S4	126.6(7)
C55-C56-H56	119.8	C63-C68-S4	113.0(6)
C56-C57-C58	120.1(8)	C78-C69-C70	123.0(6)
C56-C57-H57	120.0	C78-C69-S5	114.3(5)
C58-C57-H57	120.0	C70-C69-S5	122.4(5)
C59-C58-C57	120.0(9)	C75-C70-C69	117.2(6)
C59-C58-H58	120.0	C75-C70-C71	120.1(6)
C57-C58-H58	120.0	C69-C70-C71	122.2(6)
C58-C59-C60	121.5(9)	C72-C71-C70	120.3(6)
C58-C59-H59	119.3	C72-C71-H71	119.8
C60-C59-H59	119.3	C70-C71-H71	119.8
C55-C60-C59	119.2(8)	C71-C72-C73	120.1(6)
C55-C60-C61	117.5(7)	C71-C72-H72	119.9
C59-C60-C61	123.0(8)	C73-C72-H72	119.9
C62-C61-C60	123.0(7)	C74-C73-C72	120.1(7)
C62-C61-S4	113.0(6)	C74-C73-H73	120.0
C60-C61-S4	123.2(6)	C72-C73-H73	120.0
C61-C62-C54	118.8(7)	C73-C74-C75	122.5(6)
C61-C62-C63	111.6(6)	C73-C74-H74	118.7
C54-C62-C63	129.3(7)	C75-C74-H74	118.7
C64-C63-C68	117.7(7)	C74-C75-C70	116.8(6)
C64-C63-C62	131.6(6)	C74-C75-C76	123.9(6)
C68-C63-C62	110.5(7)	C70-C75-C76	119.3(6)
C65-C64-C63	121.1(7)	C77-C76-C85	118.4(6)
C65-C64-H64	119.5	C77-C76-C75	121.4(6)
C63-C64-H64	119.5	C85-C76-C75	120.2(6)
C64-C65-C66	121.1(9)	C76-C77-C88	118.4(6)
C64-C65-H65	119.4	C76-C77-C78	117.1(6)
C66-C65-H65	119.4	C88-C77-C78	124.4(6)
C67-C66-C65	119.5(8)	C69-C78-C77	119.2(6)
C67-C66-H66	120.2	C69-C78-C79	110.0(6)
C65-C66-H66	120.2	C77-C78-C79	130.6(6)
C66-C67-C68	120.2(8)	C84-C79-C80	117.0(5)
C66-C67-H67	119.9	C84-C79-C78	111.9(6)
C68-C67-H67	119.9	C80-C79-C78	130.9(6)
C67-C68-C63	120.3(8)	C81-C80-C79	119.3(6)

C81-C80-H80	120.3	C91-C92-H92	120.1
C79-C80-H80	120.3	C93-C92-H92	120.1
C80-C81-C82	121.6(6)	C92-C93-C94	119.1(7)
C80-C81-H81	119.2	C92-C93-H93	120.5
C82-C81-H81	119.2	C94-C93-H93	120.5
C83-C82-C81	120.4(6)	C89-C94-C93	121.0(6)
C83-C82-H82	119.8	C89-C94-C95	118.2(6)
C81-C82-H82	119.8	C93-C94-C95	120.4(6)
C82-C83-C84	118.1(6)	C96-C95-C94	121.7(6)
C82-C83-H83	120.9	C96-C95-S6	115.3(5)
C84-C83-H83	120.9	C94-C95-S6	122.4(5)
C83-C84-C79	123.2(6)	C95-C96-C88	120.0(6)
C83-C84-S5	124.1(5)	C95-C96-C97	109.9(6)
C79-C84-S5	112.6(5)	C88-C96-C97	129.9(6)
C86-C85-C76	122.3(6)	C102-C97-C98	117.9(6)
C86-C85-H85	118.9	C102-C97-C96	111.4(6)
C76-C85-H85	118.9	C98-C97-C96	130.5(6)
C85-C86-C87	121.2(6)	C99-C98-C97	118.9(7)
C85-C86-H86	119.4	C99-C98-H98	120.5
C87-C86-H86	119.4	C97-C98-H98	120.5
C86-C87-C88	117.4(6)	C98-C99-C100	122.2(6)
C86-C87-C89	121.2(6)	C98-C99-H99	118.9
C88-C87-C89	121.3(6)	C100-C99-H99	118.9
C87-C88-C77	119.7(6)	C101-C100-C99	119.5(7)
C87-C88-C96	115.7(6)	C101-C100-H100	120.2
C77-C88-C96	124.5(6)	C99-C100-H100	120.2
C94-C89-C90	117.9(6)	C102-C101-C100	118.0(7)
C94-C89-C87	119.5(6)	C102-C101-H101	121.0
C90-C89-C87	122.6(6)	C100-C101-H101	121.0
C91-C90-C89	121.5(7)	C101-C102-C97	123.3(6)
C91-C90-H90	119.3	C101-C102-S6	123.7(6)
C89-C90-H90	119.3	C97-C102-S6	112.9(5)
C90-C91-C92	120.7(6)	C16-S1-C1	91.2(3)
C90-C91-H91	119.6	C34-S2-C27	90.8(3)
C92-C91-H91	119.6	C50-S3-C35	90.9(4)
C91-C92-C93	119.7(6)	C68-S4-C61	91.6(4)

C69-S5-C84	90.5(3)	C95-S6-C102	90.0(3)

Table 7.11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7.14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	27(4)	25(4)	32(4)	-1(3)	-3(3)	-5(3)
C2	33(5)	38(5)	40(5)	6(4)	4(4)	-4(4)
C3	33(4)	39(4)	38(4)	12(4)	-2(4)	-5(4)
C4	42(5)	48(5)	33(4)	9(4)	-5(4)	-3(4)
C5	44(5)	47(5)	54(5)	25(4)	-15(4)	1(4)
C6	35(5)	27(4)	55(5)	14(4)	-1(4)	6(3)
C7	19(4)	34(4)	41(4)	4(4)	10(3)	-8(3)
C8	29(4)	30(4)	37(4)	0(4)	-2(3)	1(3)
C9	31(4)	30(4)	23(4)	2(3)	1(3)	-1(3)
C10	33(4)	31(4)	30(4)	-3(3)	-1(3)	0(3)
C11	32(4)	23(4)	30(4)	-5(3)	-3(3)	-2(3)
C12	25(4)	29(4)	33(4)	0(3)	-4(3)	-3(3)
C13	40(5)	44(5)	42(5)	10(4)	-6(4)	0(4)
C14	47(5)	34(5)	53(5)	12(4)	-12(4)	-10(4)
C15	44(5)	26(4)	45(5)	-3(4)	-7(4)	0(3)
C16	38(5)	31(4)	36(4)	3(4)	-2(3)	-6(4)
C17	34(4)	24(4)	44(5)	2(4)	-2(4)	-2(3)
C18	37(5)	23(4)	45(5)	-7(3)	7(4)	-6(3)
C19	31(4)	24(4)	32(4)	0(3)	6(3)	-3(3)
C20	27(4)	25(4)	30(4)	-1(3)	4(3)	-1(3)
C21	29(4)	36(4)	39(4)	2(4)	3(4)	-13(4)
C22	35(5)	31(4)	49(5)	-4(4)	7(4)	-11(3)
C23	33(5)	38(5)	49(5)	-11(4)	0(4)	-14(4)
C24	35(5)	46(5)	47(5)	-7(4)	-4(4)	-3(4)
C25	29(4)	34(4)	45(5)	6(4)	-9(4)	-7(3)
C26	27(4)	39(5)	32(4)	-4(4)	7(3)	-8(4)
C27	29(4)	30(4)	38(4)	3(3)	-4(4)	-1(3)
C28	29(4)	22(4)	39(4)	6(3)	-1(4)	-3(3)
C29	29(4)	31(4)	30(4)	-2(3)	3(3)	-6(3)
C30	26(4)	38(5)	41(5)	3(4)	5(3)	7(3)
C31	43(5)	42(5)	45(5)	-8(4)	-2(4)	0(4)

C32	50(5)	33(4)	54(5)	-9(4)	-2(4)	16(4)
C33	46(5)	41(5)	54(5)	4(4)	-15(4)	13(4)
C34	49(5)	27(4)	43(5)	5(4)	-7(4)	0(4)
C35	31(4)	36(4)	36(4)	-6(4)	-7(3)	-7(4)
C36	26(4)	25(4)	52(5)	-12(4)	-11(4)	5(3)
C37	39(5)	28(4)	41(5)	-10(4)	-12(4)	5(4)
C38	32(5)	32(5)	60(5)	-23(4)	-16(4)	6(4)
C39	32(5)	27(4)	63(6)	-3(4)	-10(4)	-1(4)
C40	37(5)	29(4)	49(5)	-7(4)	-12(4)	-2(4)
C41	28(4)	20(4)	47(5)	-8(4)	-12(4)	-4(3)
C42	26(4)	27(4)	38(5)	-13(4)	-9(4)	1(3)
C43	29(4)	20(4)	50(5)	-11(4)	-17(4)	4(3)
C44	42(5)	31(4)	29(4)	-3(4)	-3(4)	2(4)
C45	41(5)	22(4)	43(5)	2(4)	-17(4)	-8(3)
C46	37(5)	30(5)	50(5)	-1(4)	-19(4)	-2(4)
C47	55(6)	44(5)	58(6)	1(5)	-17(5)	6(4)
C48	65(6)	44(6)	60(6)	11(5)	-20(5)	-5(5)
C49	61(6)	69(6)	34(5)	13(5)	-9(4)	-7(5)
C50	53(5)	35(5)	44(5)	-3(4)	-12(4)	3(4)
C51	20(4)	31(4)	54(5)	-7(4)	-8(4)	-7(3)
C52	25(4)	38(5)	47(5)	-3(4)	-9(4)	-14(4)
C53	22(4)	27(4)	55(5)	-7(4)	-7(4)	-1(3)
C54	31(5)	18(4)	49(5)	-1(3)	-6(4)	-13(3)
C55	39(5)	30(4)	54(5)	-11(4)	2(4)	-13(4)
C56	32(5)	43(5)	84(7)	-22(5)	2(5)	-11(4)
C57	37(5)	68(6)	79(7)	-33(6)	9(5)	-19(5)
C58	35(5)	45(6)	117(9)	-37(6)	13(6)	-13(4)
C59	33(5)	26(5)	117(8)	-22(5)	2(5)	-6(4)
C60	41(5)	25(4)	84(7)	-18(5)	-7(5)	-5(4)
C61	33(5)	22(4)	88(7)	5(4)	-13(5)	-8(4)
C62	30(5)	18(4)	70(6)	0(4)	-12(4)	-4(3)
C63	37(5)	29(4)	61(6)	14(4)	-23(4)	-12(4)
C64	53(5)	33(5)	57(5)	3(4)	-25(4)	1(4)
C65	70(6)	57(6)	58(6)	20(5)	-30(5)	-11(5)
C66	84(8)	79(7)	61(7)	19(6)	-34(6)	-23(6)
C67	45(6)	86(8)	97(8)	42(6)	-29(6)	3(5)

C68	43(5)	38(5)	69(6)	8(4)	-8(5)	0(4)
C69	26(4)	20(4)	41(5)	0(3)	-11(3)	-3(3)
C70	27(4)	30(4)	40(5)	9(4)	-5(3)	6(3)
C71	25(4)	20(4)	51(5)	4(4)	-11(4)	-5(3)
C72	37(5)	33(4)	42(5)	15(4)	3(4)	-3(4)
C73	31(4)	34(4)	41(5)	5(4)	-8(4)	-3(4)
C74	33(4)	24(4)	46(5)	4(4)	-13(4)	-3(3)
C75	27(4)	18(4)	39(5)	8(3)	-9(4)	0(3)
C76	30(4)	23(4)	35(5)	1(3)	-11(4)	3(3)
C77	26(4)	17(4)	41(5)	-1(3)	-8(4)	-2(3)
C78	31(4)	21(4)	35(4)	5(3)	-2(3)	3(3)
C79	21(4)	31(4)	34(4)	-1(3)	-8(3)	-1(3)
C80	40(5)	21(4)	40(5)	2(3)	-9(4)	9(3)
C81	41(5)	27(4)	33(4)	4(3)	-9(4)	2(3)
C82	36(5)	43(5)	28(4)	2(4)	-6(3)	4(4)
C83	40(5)	31(4)	38(5)	1(4)	-13(4)	-1(4)
C84	36(4)	24(4)	31(4)	10(3)	-5(3)	-5(3)
C85	39(5)	23(4)	31(4)	7(3)	-11(3)	6(3)
C86	24(4)	34(4)	36(5)	-2(3)	-7(3)	7(3)
C87	22(4)	21(4)	35(4)	-6(3)	-4(3)	4(3)
C88	28(4)	23(4)	37(4)	10(3)	-8(4)	9(3)
C89	24(4)	17(4)	43(5)	5(3)	-6(4)	0(3)
C90	30(4)	25(4)	44(4)	1(4)	-8(3)	-2(3)
C91	36(5)	24(4)	42(5)	-3(3)	-4(4)	0(4)
C92	34(5)	23(4)	52(5)	4(4)	-10(4)	-1(3)
C93	34(5)	34(4)	43(5)	13(4)	-13(4)	-4(4)
C94	28(4)	25(4)	41(5)	3(4)	-2(4)	-1(3)
C95	28(4)	27(4)	36(4)	-2(3)	-10(3)	-2(3)
C96	26(4)	17(4)	41(4)	6(3)	-8(3)	-3(3)
C97	28(4)	24(4)	33(4)	-3(3)	-8(3)	5(3)
C98	44(5)	20(4)	42(4)	0(4)	-11(4)	0(3)
C99	37(5)	20(4)	47(5)	5(4)	-7(4)	1(3)
C100	44(5)	28(4)	48(5)	2(4)	-5(4)	1(4)
C101	38(5)	39(5)	39(4)	5(4)	-4(4)	9(4)
C102	26(4)	17(4)	49(5)	0(3)	-3(4)	4(3)
S1	44(1)	31(1)	43(1)	2(1)	-10(1)	-9(1)

S2	40(1)	33(1)	44(1)	2(1)	-9(1)	6(1)
S3	55(1)	46(1)	45(1)	-4(1)	-2(1)	2(1)
S4	44(1)	38(1)	113(2)	20(1)	-10(1)	10(1)
S5	39(1)	29(1)	43(1)	2(1)	-8(1)	-7(1)
S6	38(1)	27(1)	44(1)	1(1)	1(1)	-1(1)

Table 7.12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7.14.**

	x	y	z	U(eq)
H3	6134	1099	6164	44
H4	7026	187	6440	49
H5	6405	-800	6184	58
H6	4887	-868	5667	47
H12	2858	1646	4509	35
H13	3244	2657	4280	51
H14	4452	3405	4643	54
H15	5374	3154	5219	46
H17	3553	-895	5216	41
H18	2122	-937	4691	42
H22	796	-962	4228	46
H23	-900	-998	3750	48
H24	-2257	-113	3587	52
H25	-1835	836	3887	44
H30	1597	1554	5495	42
H31	641	2448	5770	52
H32	-985	3089	5449	55
H33	-1871	2808	4868	57
H37	8041	2319	6193	44
H38	8711	1426	6511	50
H39	7748	1217	7083	49
H40	6112	1906	7343	46
H46	4480	4958	6678	47
H47	5032	5829	6332	64
H48	6356	5736	5807	68
H49	7381	4768	5650	66
H51	4765	2558	7569	42
H52	3377	3323	7822	45
H56	2099	3999	8036	64
H57	479	4731	8262	74
H58	-564	5499	7868	78

H59	-52	5506	7261	70
H64	3349	3416	6166	58
H65	2577	3434	5562	75
H66	967	4206	5343	90
H67	-39	4903	5752	92
H71	7948	3827	2212	39
H72	8663	3745	1610	45
H73	7799	2922	1239	43
H74	6167	2206	1463	42
H80	4835	1703	3334	40
H81	5495	1848	3945	41
H82	6721	2747	4141	43
H83	7625	3445	3713	44
H85	4737	1594	1665	37
H86	3320	822	1900	38
H90	1985	156	2104	40
H91	495	-592	2347	41
H92	-331	-491	2943	44
H93	322	399	3296	45
H98	3314	3176	2827	43
H99	2561	4001	3191	42
H100	1262	3828	3720	48
H101	477	2803	3860	46

Table 7.13. Torsion angles [°] for **7.14**.

C10-C1-C2-C3	179.6(6)	C9-C10-C11-C16	179.4(6)
S1-C1-C2-C3	7.7(9)	C16-C11-C12-C13	-4.0(9)
C10-C1-C2-C7	5.9(10)	C10-C11-C12-C13	-178.9(6)
S1-C1-C2-C7	-166.1(5)	C11-C12-C13-C14	0.7(10)
C7-C2-C3-C4	2.9(10)	C12-C13-C14-C15	1.9(11)
C1-C2-C3-C4	-170.6(6)	C13-C14-C15-C16	-1.0(11)
C2-C3-C4-C5	-0.8(10)	C14-C15-C16-C11	-2.5(10)
C3-C4-C5-C6	-0.8(11)	C14-C15-C16-S1	174.4(6)
C4-C5-C6-C7	0.4(11)	C12-C11-C16-C15	5.0(10)
C3-C2-C7-C6	-3.3(10)	C10-C11-C16-C15	-179.1(6)
C1-C2-C7-C6	170.6(6)	C12-C11-C16-S1	-172.3(5)
C3-C2-C7-C8	175.9(6)	C10-C11-C16-S1	3.5(7)
C1-C2-C7-C8	-10.2(9)	C9-C8-C17-C18	-0.9(10)
C5-C6-C7-C2	1.6(10)	C7-C8-C17-C18	-178.9(6)
C5-C6-C7-C8	-177.6(6)	C8-C17-C18-C19	-8.6(10)
C2-C7-C8-C9	-0.2(9)	C17-C18-C19-C20	2.0(10)
C6-C7-C8-C9	178.9(6)	C17-C18-C19-C21	-177.3(6)
C2-C7-C8-C17	177.7(6)	C18-C19-C20-C28	-164.2(6)
C6-C7-C8-C17	-3.2(10)	C21-C19-C20-C28	15.1(9)
C17-C8-C9-C20	16.5(9)	C18-C19-C20-C9	13.5(9)
C7-C8-C9-C20	-165.5(6)	C21-C19-C20-C9	-167.2(6)
C17-C8-C9-C10	-163.0(6)	C8-C9-C20-C19	-22.7(9)
C7-C8-C9-C10	15.0(9)	C10-C9-C20-C19	156.7(6)
C2-C1-C10-C9	9.0(10)	C8-C9-C20-C28	154.8(6)
S1-C1-C10-C9	-178.3(5)	C10-C9-C20-C28	-25.8(10)
C2-C1-C10-C11	-165.5(6)	C20-C19-C21-C22	176.2(6)
S1-C1-C10-C11	7.1(7)	C18-C19-C21-C22	-4.5(10)
C8-C9-C10-C1	-19.3(9)	C20-C19-C21-C26	-4.5(9)
C20-C9-C10-C1	161.2(6)	C18-C19-C21-C26	174.8(6)
C8-C9-C10-C11	154.1(6)	C26-C21-C22-C23	-1.3(10)
C20-C9-C10-C11	-25.4(11)	C19-C21-C22-C23	178.1(6)
C1-C10-C11-C12	168.5(6)	C21-C22-C23-C24	0.6(10)
C9-C10-C11-C12	-5.4(12)	C22-C23-C24-C25	1.5(11)
C1-C10-C11-C16	-6.7(8)	C23-C24-C25-C26	-2.8(10)

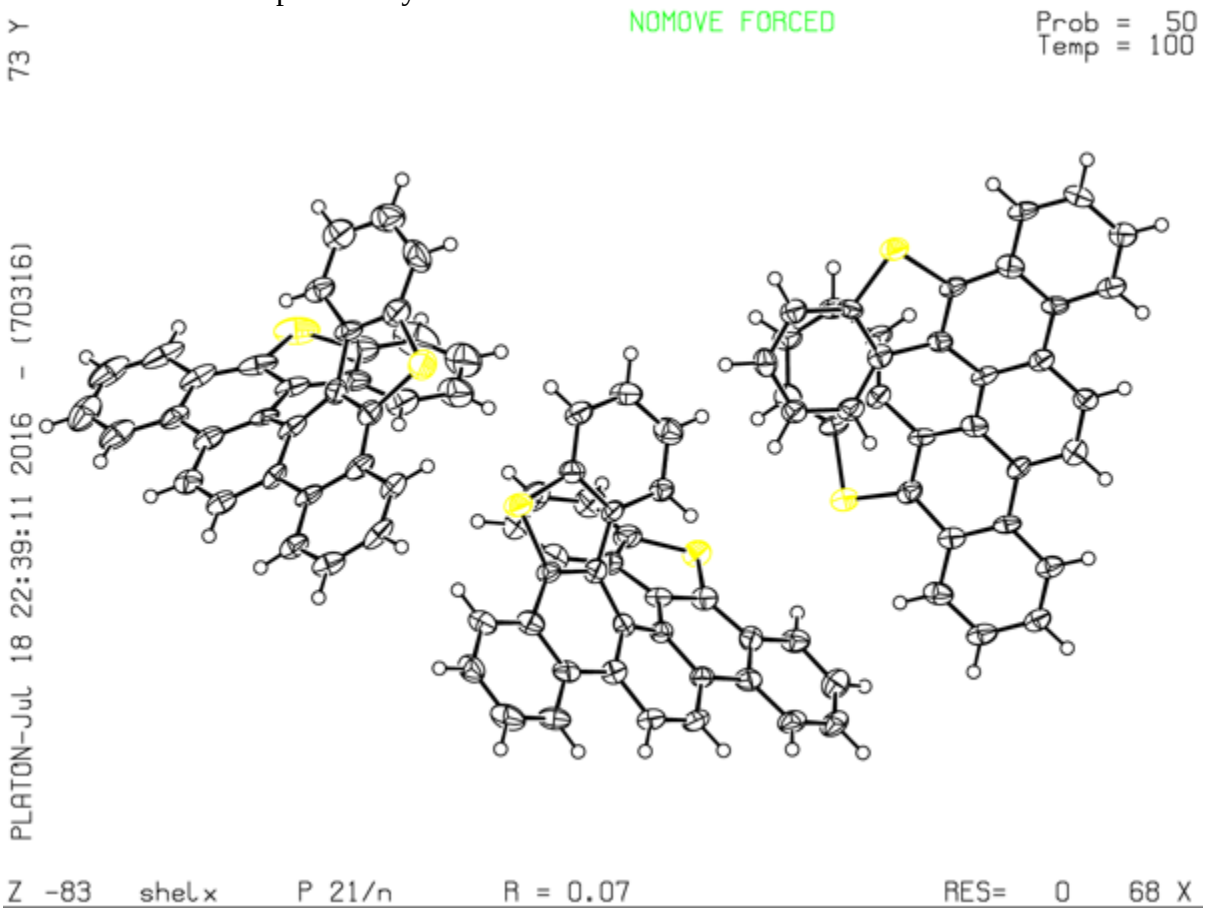
C24-C25-C26-C21	2.0(10)	S3-C35-C36-C41	166.5(4)
C24-C25-C26-C27	-173.7(6)	C41-C36-C37-C38	1.1(9)
C22-C21-C26-C25	0.0(9)	C35-C36-C37-C38	172.7(6)
C19-C21-C26-C25	-179.4(6)	C36-C37-C38-C39	0.1(10)
C22-C21-C26-C27	176.0(6)	C37-C38-C39-C40	-0.4(10)
C19-C21-C26-C27	-3.4(9)	C38-C39-C40-C41	-0.6(10)
C25-C26-C27-C28	176.0(6)	C37-C36-C41-C40	-2.1(9)
C21-C26-C27-C28	0.1(10)	C35-C36-C41-C40	-174.3(5)
C25-C26-C27-S2	5.5(9)	C37-C36-C41-C42	-179.0(6)
C21-C26-C27-S2	-170.4(5)	C35-C36-C41-C42	8.8(9)
C26-C27-C28-C20	10.7(10)	C39-C40-C41-C36	1.8(9)
S2-C27-C28-C20	-178.2(5)	C39-C40-C41-C42	178.7(6)
C26-C27-C28-C29	-163.7(6)	C36-C41-C42-C43	1.0(9)
S2-C27-C28-C29	7.4(7)	C40-C41-C42-C43	-175.8(5)
C19-C20-C28-C27	-17.9(9)	C36-C41-C42-C51	-177.3(6)
C9-C20-C28-C27	164.5(6)	C40-C41-C42-C51	5.9(9)
C19-C20-C28-C29	155.1(6)	C41-C42-C43-C54	166.9(6)
C9-C20-C28-C29	-22.4(11)	C51-C42-C43-C54	-14.7(8)
C27-C28-C29-C34	-6.1(8)	C41-C42-C43-C44	-15.1(8)
C20-C28-C29-C34	-179.5(6)	C51-C42-C43-C44	163.2(5)
C27-C28-C29-C30	169.3(6)	C36-C35-C44-C43	-9.7(10)
C20-C28-C29-C30	-4.2(11)	S3-C35-C44-C43	178.6(4)
C34-C29-C30-C31	-1.6(9)	C36-C35-C44-C45	166.1(6)
C28-C29-C30-C31	-176.7(6)	S3-C35-C44-C45	-5.7(7)
C29-C30-C31-C32	-1.6(10)	C54-C43-C44-C35	-163.0(6)
C30-C31-C32-C33	3.3(11)	C42-C43-C44-C35	19.2(9)
C31-C32-C33-C34	-1.6(11)	C54-C43-C44-C45	22.1(10)
C32-C33-C34-C29	-1.7(11)	C42-C43-C44-C45	-155.7(6)
C32-C33-C34-S2	175.0(6)	C35-C44-C45-C46	-169.1(6)
C30-C29-C34-C33	3.3(10)	C43-C44-C45-C46	6.0(11)
C28-C29-C34-C33	179.2(6)	C35-C44-C45-C50	6.4(8)
C30-C29-C34-S2	-173.7(5)	C43-C44-C45-C50	-178.4(6)
C28-C29-C34-S2	2.2(7)	C50-C45-C46-C47	2.7(9)
C44-C35-C36-C37	-176.6(6)	C44-C45-C46-C47	178.1(6)
S3-C35-C36-C37	-5.4(9)	C45-C46-C47-C48	1.1(10)
C44-C35-C36-C41	-4.6(9)	C46-C47-C48-C49	-3.7(11)

C47-C48-C49-C50	2.2(11)	C59-C60-C61-C62	-179.3(7)
C48-C49-C50-C45	1.8(11)	C55-C60-C61-S4	164.2(5)
C48-C49-C50-S3	-173.7(6)	C59-C60-C61-S4	-9.8(10)
C46-C45-C50-C49	-4.2(10)	C60-C61-C62-C54	-9.6(10)
C44-C45-C50-C49	179.6(6)	S4-C61-C62-C54	179.9(5)
C46-C45-C50-S3	171.9(5)	C60-C61-C62-C63	165.1(6)
C44-C45-C50-S3	-4.4(7)	S4-C61-C62-C63	-5.4(7)
C43-C42-C51-C52	-2.1(9)	C43-C54-C62-C61	-162.6(6)
C41-C42-C51-C52	176.3(6)	C53-C54-C62-C61	20.9(9)
C42-C51-C52-C53	10.4(9)	C43-C54-C62-C63	23.8(10)
C51-C52-C53-C54	-1.6(9)	C53-C54-C62-C63	-152.7(7)
C51-C52-C53-C55	177.3(6)	C61-C62-C63-C64	-170.8(7)
C42-C43-C54-C53	23.7(8)	C54-C62-C63-C64	3.2(12)
C44-C43-C54-C53	-154.1(6)	C61-C62-C63-C68	4.3(8)
C42-C43-C54-C62	-152.7(6)	C54-C62-C63-C68	178.3(7)
C44-C43-C54-C62	29.5(9)	C68-C63-C64-C65	2.1(11)
C52-C53-C54-C43	-15.5(9)	C62-C63-C64-C65	176.9(7)
C55-C53-C54-C43	165.6(6)	C63-C64-C65-C66	0.4(12)
C52-C53-C54-C62	161.2(5)	C64-C65-C66-C67	-3.2(13)
C55-C53-C54-C62	-17.8(8)	C65-C66-C67-C68	3.4(14)
C52-C53-C55-C60	-175.7(6)	C66-C67-C68-C63	-0.9(13)
C54-C53-C55-C60	3.2(9)	C66-C67-C68-S4	-176.7(7)
C52-C53-C55-C56	6.4(10)	C64-C63-C68-C67	-1.8(11)
C54-C53-C55-C56	-174.7(6)	C62-C63-C68-C67	-177.7(7)
C60-C55-C56-C57	0.8(10)	C64-C63-C68-S4	174.5(5)
C53-C55-C56-C57	178.8(6)	C62-C63-C68-S4	-1.3(7)
C55-C56-C57-C58	-1.8(11)	C78-C69-C70-C75	-5.7(9)
C56-C57-C58-C59	1.2(11)	S5-C69-C70-C75	167.5(5)
C57-C58-C59-C60	0.5(12)	C78-C69-C70-C71	-177.2(6)
C56-C55-C60-C59	0.9(10)	S5-C69-C70-C71	-4.0(9)
C53-C55-C60-C59	-177.2(6)	C75-C70-C71-C72	-2.6(9)
C56-C55-C60-C61	-173.4(6)	C69-C70-C71-C72	168.7(6)
C53-C55-C60-C61	8.5(10)	C70-C71-C72-C73	1.2(9)
C58-C59-C60-C55	-1.5(11)	C71-C72-C73-C74	1.2(9)
C58-C59-C60-C61	172.4(7)	C72-C73-C74-C75	-2.4(10)
C55-C60-C61-C62	-5.3(10)	C73-C74-C75-C70	1.0(9)

C73-C74-C75-C76	179.6(6)	C77-C76-C85-C86	-2.3(9)
C69-C70-C75-C74	-170.2(5)	C75-C76-C85-C86	177.4(6)
C71-C70-C75-C74	1.5(9)	C76-C85-C86-C87	8.4(9)
C69-C70-C75-C76	11.0(8)	C85-C86-C87-C88	-0.7(9)
C71-C70-C75-C76	-177.3(5)	C85-C86-C87-C89	-180.0(6)
C74-C75-C76-C77	180.0(6)	C86-C87-C88-C77	-12.7(8)
C70-C75-C76-C77	-1.4(9)	C89-C87-C88-C77	166.6(5)
C74-C75-C76-C85	0.3(9)	C86-C87-C88-C96	164.1(5)
C70-C75-C76-C85	178.9(5)	C89-C87-C88-C96	-16.6(8)
C85-C76-C77-C88	-11.0(8)	C76-C77-C88-C87	18.6(8)
C75-C76-C77-C88	169.3(5)	C78-C77-C88-C87	-158.4(6)
C85-C76-C77-C78	166.2(5)	C76-C77-C88-C96	-157.9(6)
C75-C76-C77-C78	-13.5(8)	C78-C77-C88-C96	25.1(9)
C70-C69-C78-C77	-9.4(9)	C86-C87-C89-C94	-179.6(6)
S5-C69-C78-C77	176.9(4)	C88-C87-C89-C94	1.2(9)
C70-C69-C78-C79	165.2(6)	C86-C87-C89-C90	1.4(9)
S5-C69-C78-C79	-8.5(7)	C88-C87-C89-C90	-177.8(6)
C76-C77-C78-C69	18.7(8)	C94-C89-C90-C91	-0.8(9)
C88-C77-C78-C69	-164.2(6)	C87-C89-C90-C91	178.2(6)
C76-C77-C78-C79	-154.6(6)	C89-C90-C91-C92	-0.6(10)
C88-C77-C78-C79	22.5(10)	C90-C91-C92-C93	0.9(9)
C69-C78-C79-C84	8.3(7)	C91-C92-C93-C94	0.2(9)
C77-C78-C79-C84	-178.0(6)	C90-C89-C94-C93	1.9(9)
C69-C78-C79-C80	-166.8(6)	C87-C89-C94-C93	-177.1(6)
C77-C78-C79-C80	7.0(11)	C90-C89-C94-C95	-170.7(5)
C84-C79-C80-C81	4.2(9)	C87-C89-C94-C95	10.2(9)
C78-C79-C80-C81	179.1(6)	C92-C93-C94-C89	-1.6(9)
C79-C80-C81-C82	0.6(10)	C92-C93-C94-C95	170.9(6)
C80-C81-C82-C83	-5.3(10)	C89-C94-C95-C96	-5.6(9)
C81-C82-C83-C84	4.6(10)	C93-C94-C95-C96	-178.3(6)
C82-C83-C84-C79	0.5(10)	C89-C94-C95-S6	165.4(5)
C82-C83-C84-S5	-175.2(5)	C93-C94-C95-S6	-7.3(8)
C80-C79-C84-C83	-4.9(9)	C94-C95-C96-C88	-10.6(9)
C78-C79-C84-C83	179.3(6)	S6-C95-C96-C88	177.7(4)
C80-C79-C84-S5	171.3(5)	C94-C95-C96-C97	164.4(5)
C78-C79-C84-S5	-4.6(7)	S6-C95-C96-C97	-7.3(7)

C87-C88-C96-C95	21.2(8)	C2-C1-S1-C16	168.3(6)
C77-C88-C96-C95	-162.2(6)	C33-C34-S2-C27	-175.4(7)
C87-C88-C96-C97	-152.6(6)	C29-C34-S2-C27	1.6(5)
C77-C88-C96-C97	24.0(10)	C28-C27-S2-C34	-5.3(5)
C95-C96-C97-C102	6.5(7)	C26-C27-S2-C34	166.1(6)
C88-C96-C97-C102	-179.2(6)	C49-C50-S3-C35	176.9(7)
C95-C96-C97-C98	-167.5(6)	C45-C50-S3-C35	1.1(5)
C88-C96-C97-C98	6.8(11)	C44-C35-S3-C50	2.7(5)
C102-C97-C98-C99	3.2(9)	C36-C35-S3-C50	-169.3(5)
C96-C97-C98-C99	176.9(6)	C67-C68-S4-C61	174.7(7)
C97-C98-C99-C100	0.9(9)	C63-C68-S4-C61	-1.4(6)
C98-C99-C100-C101	-3.7(10)	C62-C61-S4-C68	4.0(6)
C99-C100-C101-C102	2.1(9)	C60-C61-S4-C68	-166.5(6)
C100-C101-C102-C97	2.2(9)	C78-C69-S5-C84	5.2(5)
C100-C101-C102-S6	-174.1(5)	C70-C69-S5-C84	-168.5(5)
C98-C97-C102-C101	-4.9(9)	C83-C84-S5-C69	176.0(6)
C96-C97-C102-C101	-179.7(6)	C79-C84-S5-C69	-0.1(5)
C98-C97-C102-S6	171.7(4)	C96-C95-S6-C102	4.8(5)
C96-C97-C102-S6	-3.1(7)	C94-C95-S6-C102	-166.8(5)
C15-C16-S1-C1	-176.9(7)	C101-C102-S6-C95	175.9(6)
C11-C16-S1-C1	0.3(5)	C97-C102-S6-C95	-0.8(5)
C10-C1-S1-C16	-4.4(5)		

Figure 7.2. View of molecule **7.14** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Chapter 8. Synthesis of Nitrogen Doped All-Aromatic Cage Molecule and the Application as Ligand for Cyclometallated Iridium(III) Complex*

8.1 Introduction

Nitrogen atom doped polycylic aromatic hydrocarbons (N-doped PAHs)[1-4] with their long π-conjugation systems and heteroatom-metal coordination abilities lead to a broad range of applications for these molecules. Examples include organic semiconductors,[1d] solar cells,[1e] and supercapacitors.[1g] Despite these broad and longstanding interests, the shapes and topologies of N-doped PAHs are largely limited to a few motifs (Figure 8.1, top) such as N-doped spiral molecules,[1a,2] nanographenes,[1f,3] nanohoops,[4] causing a scarcity of scaffold patterns and therein limited applications. Hence, introduction of N-doped PAHs with new shapes or topologies would lead to distinct applications. Herein, we report the first example of N-doped all-aromatic cage molecule with helical strands (Figure 8.1, bottom). Furthermore, we will demonstrate this new scaffold can be applied as a ligand, wherein a cage encapsulated iridium metal is obtained to form an analogue of (*fac*)-Ir(ppy)$_3$ (ppy = 2-phenyl pyridine) which is well known as an outstanding OLED[5] light emitter and photocatalyst.[6] In the synthetic aspect, we will show that our ruthenium catalyzed transfer hydrogenative [4+2] cycloaddition reaction[7-9] is a useful strategy to prepare N-doped PAHs bearing halo-pyridines, which are able to be diversified to larger N-doped PAHs by aryl-aryl coupling reactions.

* This chapter is based on an unpublished work. Prof. Armstrong, D. W. and Mr. Hellinghausen, G. contributed to the chiral HPLC separation studies (Figure 8.2).

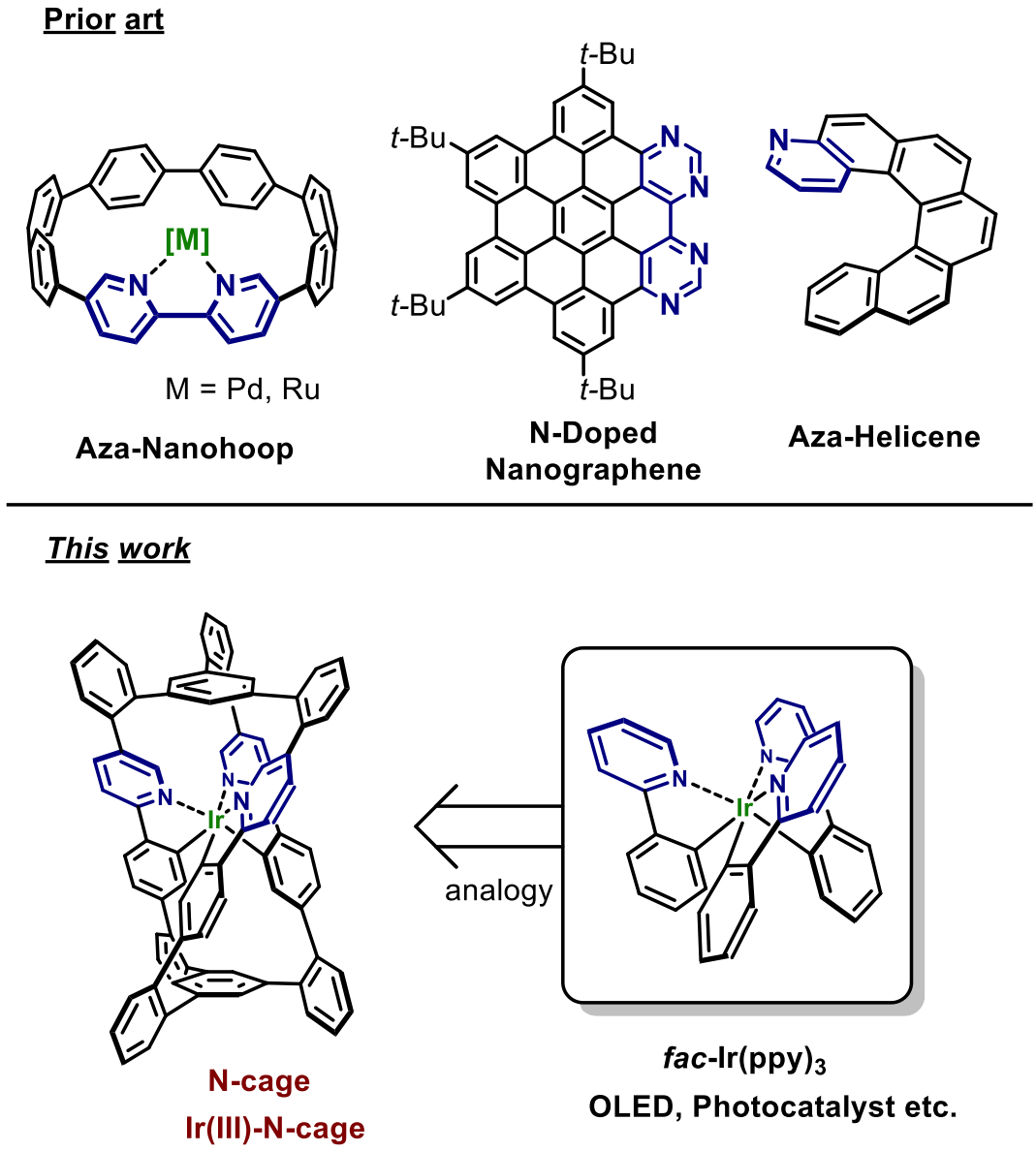
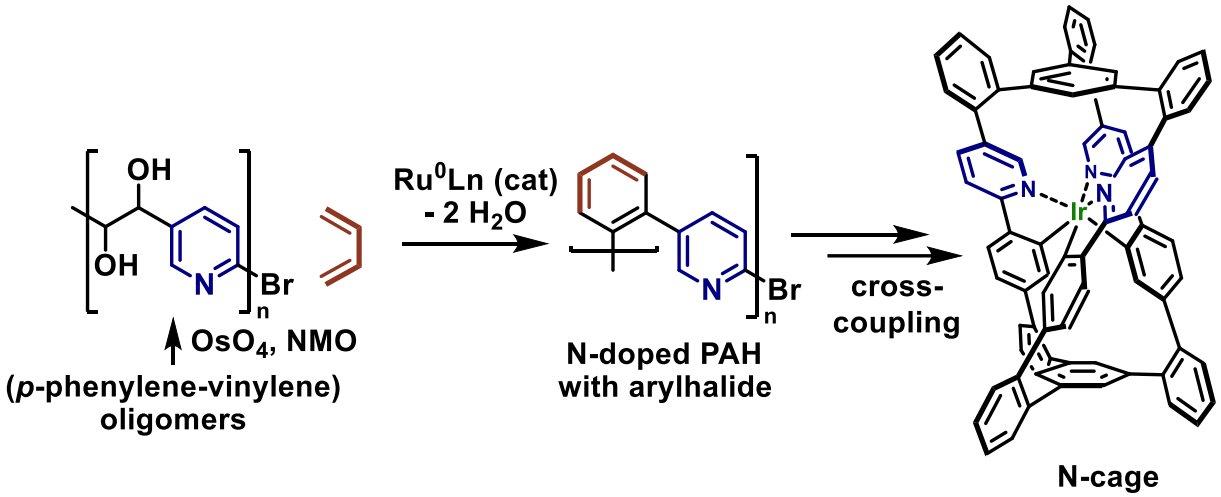


Figure 8.1. (top) Representative examples of N-doped all-aromatic PAHs based on shapes and topologies. (bottom) This work N-cage and cyclometallated Ir(III)-N-cage complex as analogue of (*fac*)-Ir(ppy)$_3$

8.2 Results and Discussion

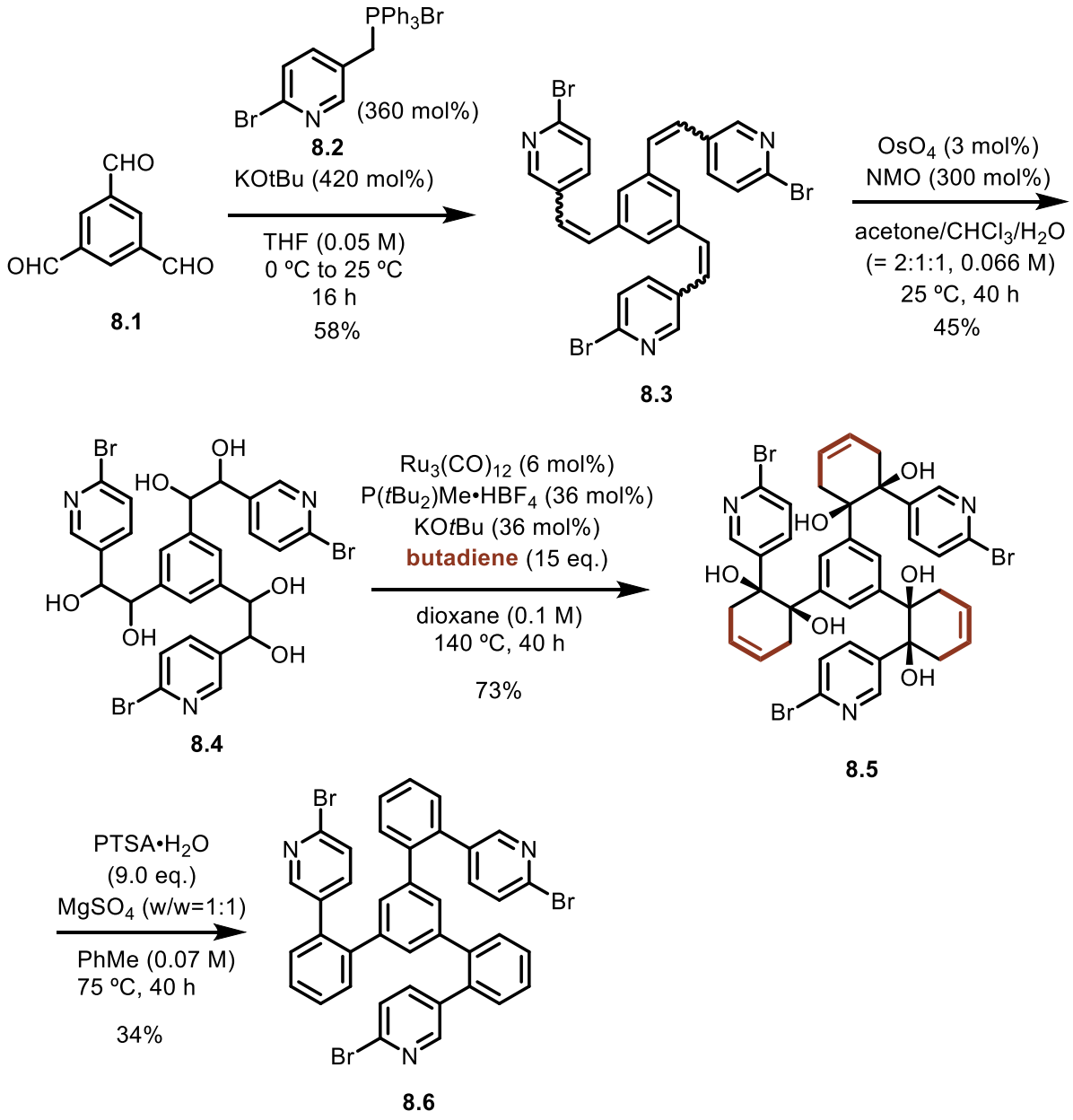
Previously our group reported the syntheses of oligo(*o,p*-phenylenes) via ruthenium catalyzed diol-diene benzannulations,[7,8] which is an orthogonal transformation to cross-coupling reactions.[9] The oligo(*o,p*-phenylenes) products with aryl halides were diversified by coupling

reactions to various PAHs including all-benzene cage molecules.[9a] During the course of exploring these reactions, we noticed that N-doped PAHs with aryl halide were much less explored compared to the corresponding PAHs while large quantities of cross-coupling reactions with heteroaryl halides have been developed.[10] Such a scarcity is due to the difficult preparations for heteroaryl halides. They are usually synthesized starting with heteroaryl halide $Ar_{Het}X_n$ (X = halide) by stoichiometric usage of organometallic reagents (Ar-[M]) under transition metal catalyzed cross-coupling reaction conditions to obtain targeted Ar-$Ar_{Het}X_{n-x}$, wherein dehalogenation and mixture of reacted/unreacted substrates are substantial problems. We envisioned that our ruthenium catalyzed benzannulation strategy was able to avoid these problems, delivering N-doped PAHs with aryl halides installed (Scheme 8.1). Thus, the synthesis of *tris*-bromide was attempted toward N-cage synthesis by a cross-coupling reaction.



Scheme 8.1. The synthetic strategy for N-cage via Ru(0) catalyzed diol-diene cycloaddition reactions

The *tris*-aldehyde (**8.1**) was subjected to Wittig olefination reaction with 2-bromopyridine containing phosphonium salt (**8.2**), delivering triene (**8.3**) as a mixture of stereoisomers in good

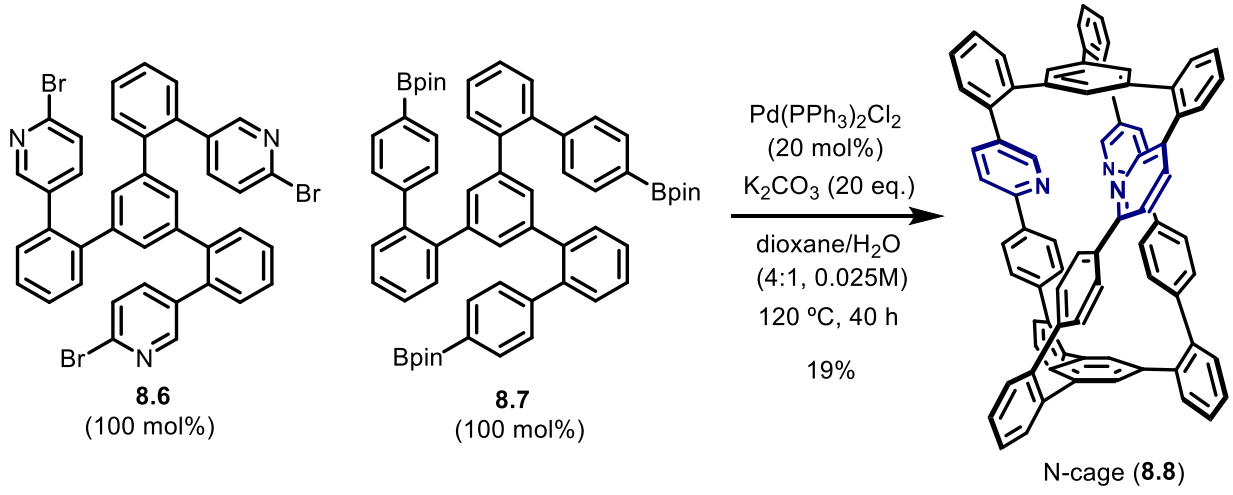


Scheme 8.2 Synthesis of *tris*-bromopyridine **8.6** from trialdehyde **8.1**. [a] Yields are of material isolated by silica gel chromatography.

yield (Scheme 8.2). Exposure of triene (**8.3**) to Upjohn dihydroxylation provided *tris*-diol (**8.4**) in 45% yield. With the *tris*-diol (**8.4**) in hand, a ruthenium catalyzed cycloaddition with 1,3-butadene was attempted. While the previous conditions with dppe or dppp ligand were ineffective, we found that P(*t*Bu)$_2$Me•HBF$_4$ ligand gave the best results. After screening of the reaction conditions, the

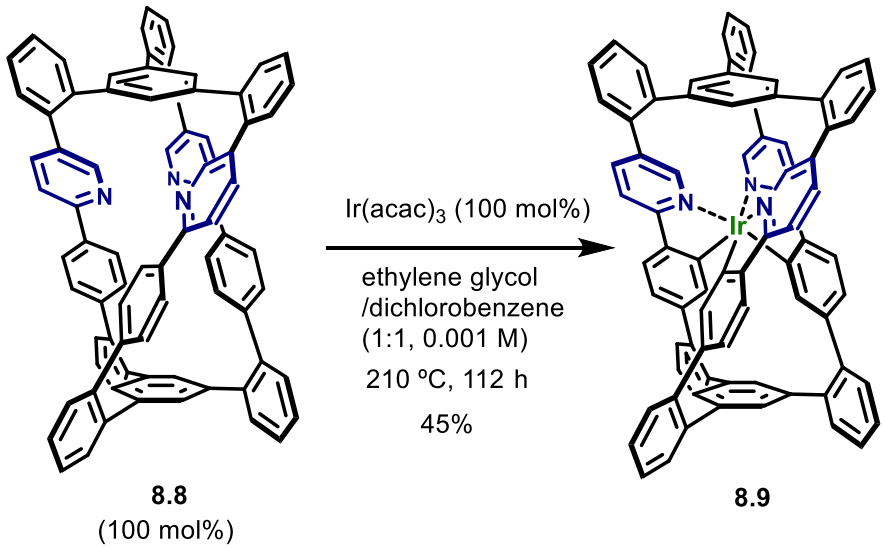
reaction of tris-diol with 6 mol% $Ru_3(CO)_{12}$ catalyst, 36 mol% P(*t*Bu)$_2$Me•HBF$_4$ ligand, 36 mol% KO*t*Bu with 15 equivalents of 1,3-butadiene in dioxane (0.1 M) at 140 ˚C gave the desired *tris*-cycloadduct (**8.5**) in 73% isolated yield. Remarkably, debrominated cycloadducts were not observed. Successively, the *tris*-cycloadduct (**8.5**) was subjected to dehydration with catalytic or stoichiometric amount of *p*-toluenesulfonic acid monohydrate (PTSA•H_2O). However, no desired aromatized compound were obtained. After screening of the additives, the reaction with $MgSO_4$ gave the desired *tris*-bromopyridine (**8.6**) in 32% yield.

As aforementioned, halopyridines are useful building blocks, which are further functionalized by Ar-Ar cross-coupling reactions delivering diverse higher N-doped PAHs (Scheme 8.1). As a demonstration, *tris*-bromopyridine (**8.6**) was subjected to a palladium catalyzed cross-coupling reaction with *tris*-Bpin (Bpin = boronic acid pinacol ester) (**8.7**) to give N-cage (**8.8**) in 19% yield after the isolation by silica gel column chromatography (Scheme 8.3). The structure was unambiguously determined by ^{1}HNMR, ^{13}CNMR, ESI-HRMS, and single crystal X-ray diffraction (See the experimental details).



Scheme 8.3. Synthesis of N-cage (**8.8**) from *tris*-bromide (**8.6**) by palladium catalyzed cross-coupling reaction. [a] Yields are of material isolated by silica gel chromatography.

It is noticeable that this novel 3-fold N-doped cage includes three 2-phenyl pyridine moieties in line strictly surrounded by top and bottom benzenes. The structure of (*fac*)-Ir(ppy)$_3$ is composed of three cyclometallated parts with all three pyridines one face, and is an important metal complex applied to OLED[9] material as well as in photocatalyst applications[10] (Figure 8.1). Exploiting the novel cage-shape and topology of the N-cage, we envisioned the synthesis of iridium encapsulated within the N-cage as an analogue of (*fac*)-Ir(ppy)$_3$,[11] in efforts to develop a compound possessing distinctive physical properties. Following previously reported condition for (*fac*)-Ir(ppy)$_3$ derivative syntheses,[11d] the N-cage (**8.8**) and Ir(acac)$_3$ were heated at 210 ˚C for 112 hours to give the desired cyclometallated iridium (III) inside of N-cage (**8.9**) in 45% yield after the



8.8
(100 mol%)

8.9

Scheme 8.4. Synthesis of Ir(III)-N-cage (**8.9**) from N-cage (**8.8**). [a] Yields are of material isolated by silica gel chromatography.

isolation by silica gel column chromatography (Scheme 8.4). The structure was unambiguously determined by 1HNMR, ESI-HRMS, and single crystal X-ray diffraction. Due to the poor solubility in any solvents, ^{13}CNMR analysis failed. Further experiments for physical properties are ongoing.

The triple strands of N-cage induce the (*M*)- and (*P*)- helicity. Expecting the future applications as chiral pure material,[12] the attempts to separate the enantiopair were explored.

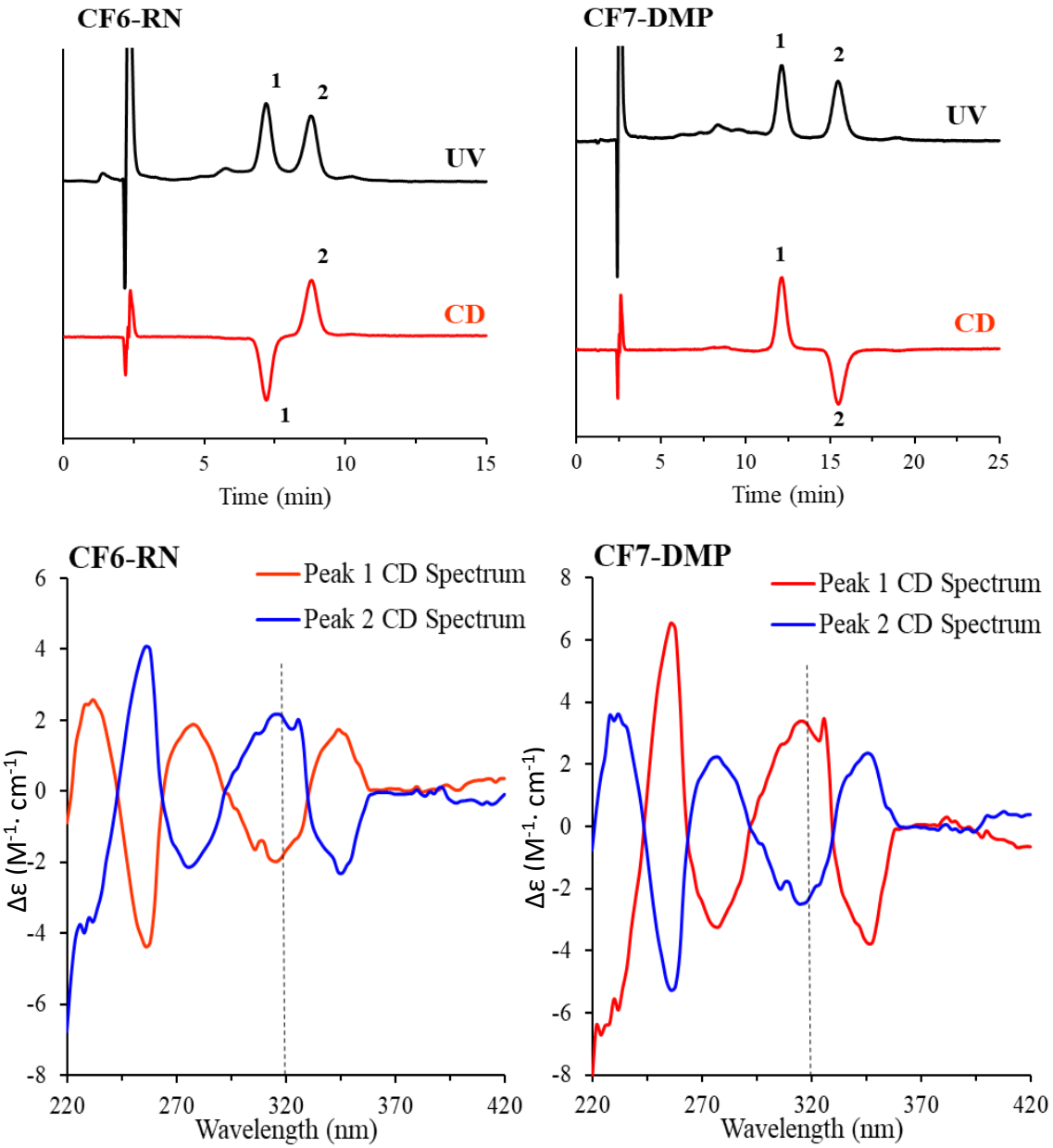


Figure 8.2. (top) UV and CD chromatograms of the enantiomeric separation of Ir(III)-N-cage (**8.9**) using the method described above with the CF6-RN (left) and CF7-DMP (right) columns at 320 nm. (bottom) CD spectra of 1st and 2nd chromatographic peaks from the enantiomeric separation of Ir(III)-N-cage (**8.9**) with the CF6-RN (left) and the CF7-DMP (right) columns using the stopped flow method described above. A dotted line was made at 320 nm in reference to the CD chromatograms illustrated above.

Interestingly, while chiral separation of Ir inside N-cage was achieved with chiral HPLC column separation, chiral separation of simple N-cage was unsuccessful. We assume that iridium inside of the N-cage fixes the strands, otherwise N-cage inverts quickly and racemizes at ambient temperature.

8.3 Summary and Future Plan

We achieved the synthesis of helical N-doped cage PAH using our ruthenium catalyzed benzannulation reactions. In addition, a novel cyclometallated Ir(III) complex was synthesized inside this N-cage. This species is analogous to the widely useful complex (*fac*)-Ir(ppy). Physical measurement for these unprecedented compounds is underway.

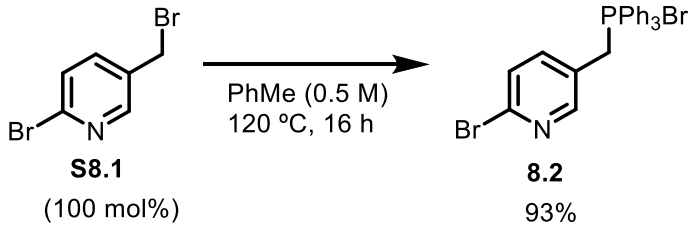
8.4 Experimental Details

General Comments

All glassware was oven dried at 120 °C overnight and cooled in a desiccator. All ruthenium catalyzed reactions were carried out in sealed pressure tubes (13 x 100 mm). Dioxane and THF were purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], tri-tert-butylphosphonium tetrafluoroborate P(*t*Bu_2)Me•HBF_4, KO*t*Bu, bis(triphenylphosphine)palladium chloride $Pd(PPh_3)Cl_2$, OsO_4, 1,3-butadiene, para-toluenesulfonic acid monohydrate PTSA•H_2O, magnesium sulfate $MgSO_4$, iridium(III) acetylacetonate $Ir(acac)_3$ were purchased from commercial suppliers. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a cerium ammonium molybdate solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded with a Bruker AVANCE III (500 MHz supported by NSF grant 1 S10 OD021508-01) spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^1H and ^{13}C are reported in parts per million (ppm) downfield from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on Agilent Technologies 6530 Accurate-Mass Q-TOF and are reported as m/z. Masses are reported for the molecular ion (M, M+H, M+Na or M+K).

Synthesis of Starting Materials

Preparation for Wittig reagent **8.2**



Benzyl bromide **S8.1** was synthesized according to known procedures[13] and the characterization data[14] match our own in all respects.

To a solution of **S8.1** (25.1 g, 100.0 mmol, 100 mol%) in toluene (200 mL) was added triphenylphosphine (34.1 g, 130.0 mmol, 130 mol%). The mixture was then refluxed for 16 hours. The solid was filtered under vacuum, and washed with toluene. The title compound **8.2** (47.8 g, 93.1 mmol) was obtained in 93% yield as a white solid.

TLC (SiO_2): R_f = 0.18 (ethylacetate : methanol = 80:20).

^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.92 (s, 1H), 7.85-7.79 (m, 6H), 7.77-7.72 (m, 3H), 7.64-7.58 (m, 6H), 7.18 (d, *J* = 8.2 Hz, 1H), 5.83 (d, *J* = 15.0 Hz, 2H) ppm.

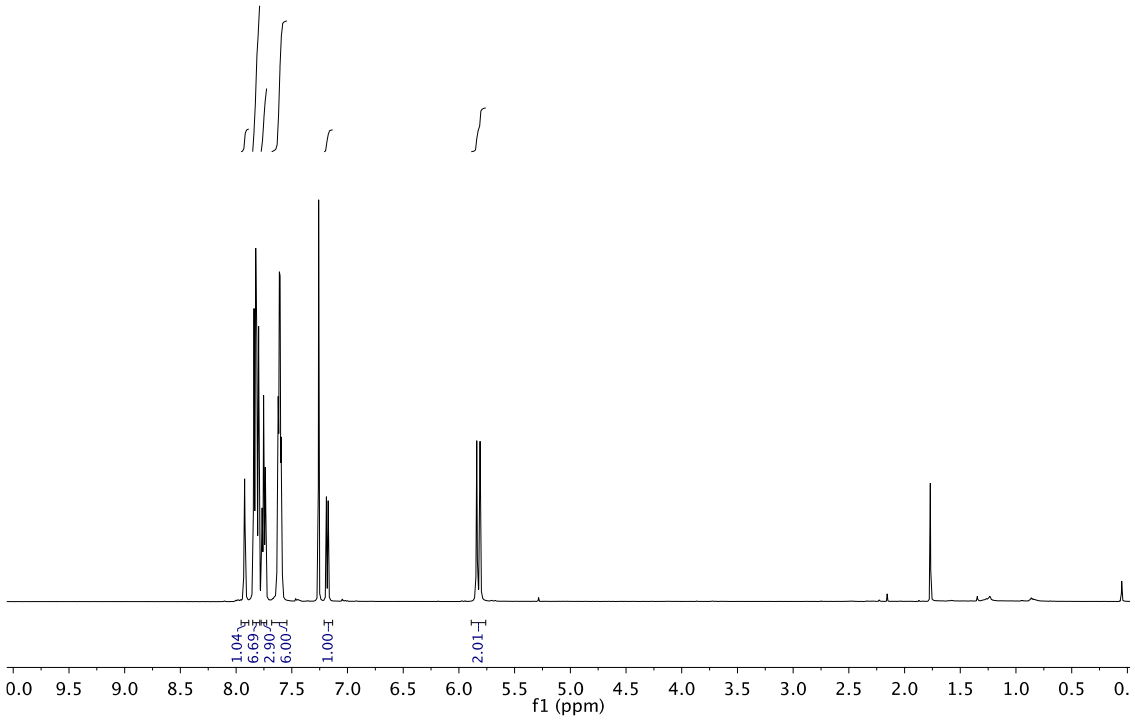
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 151.7, 142.5 , 142.1 , 135.2 , 134.5 (d), 130.4 (d), 128.1 , 124.0 , 117.1 (d), 27.0 (d) ppm.

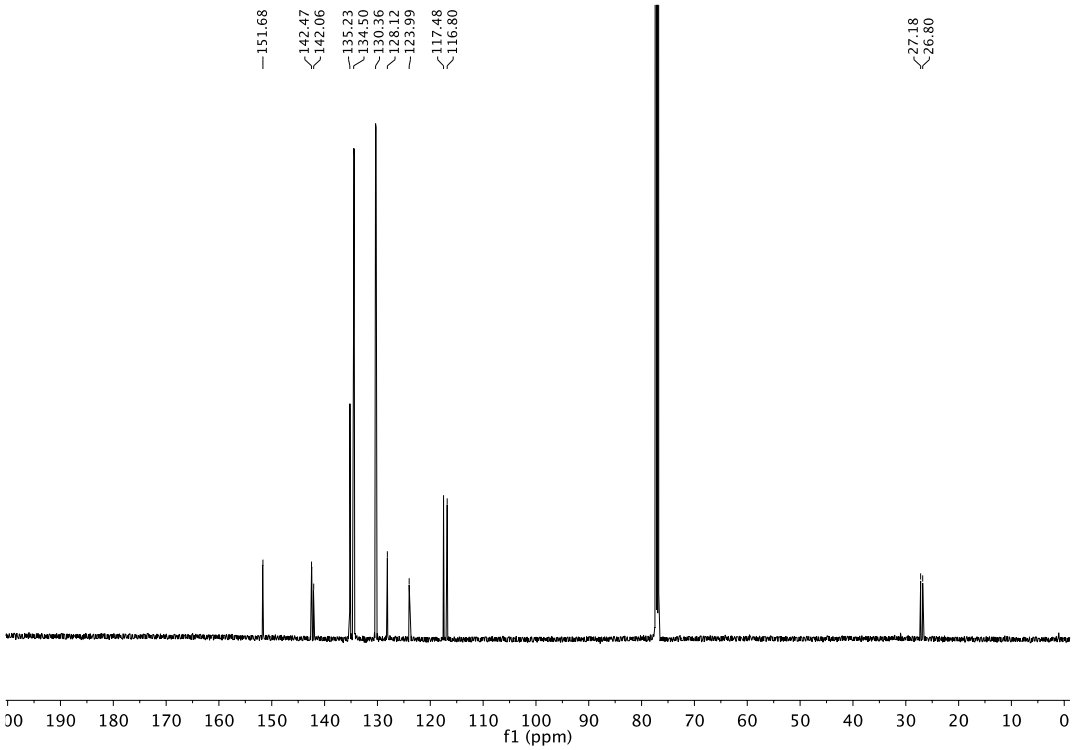
^{31}P NMR: (160 MHz, $CDCl_3$): δ = 23.9 ppm.

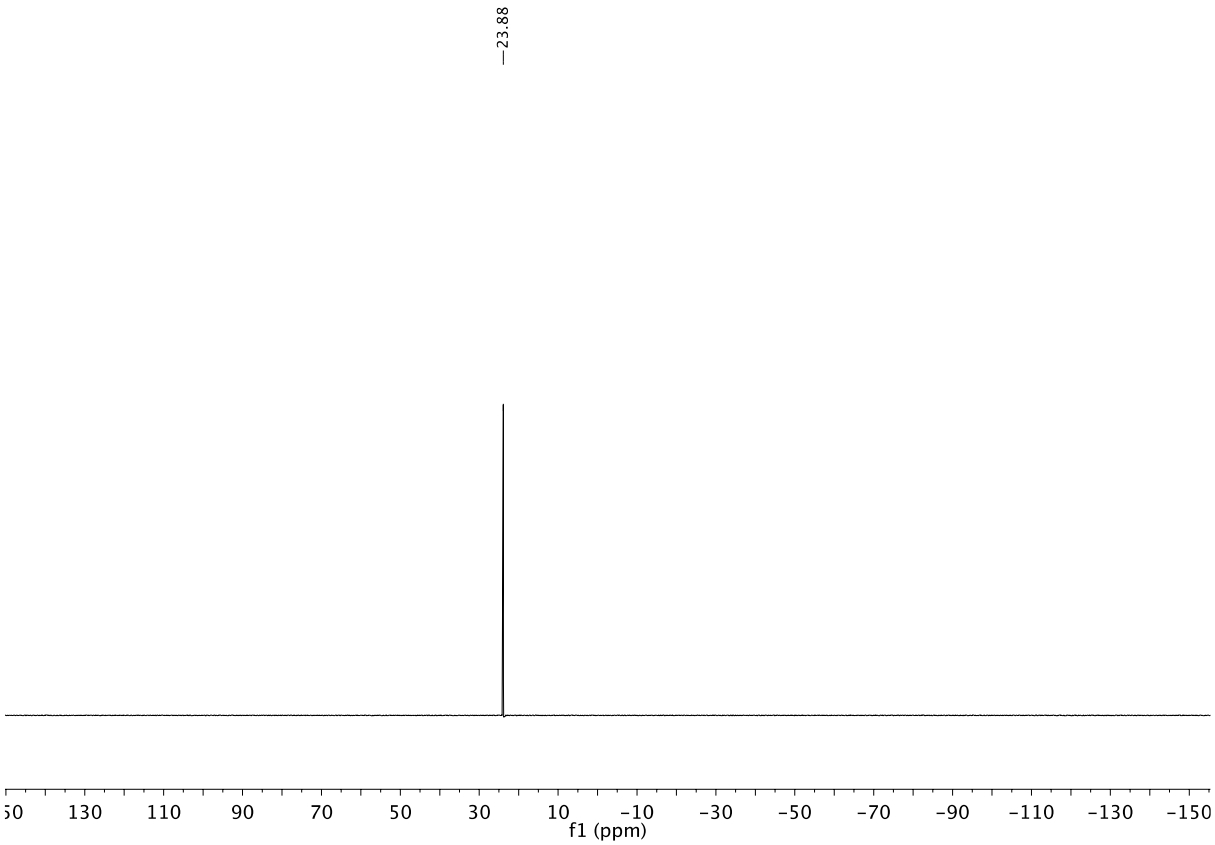
MP: >300 °C.

HRMS: (ESI) Calculated for $C_{24}H_{20}Br_2NP$ $[M\text{-}Br]^+$ = 434.0494, Found 434.0501.

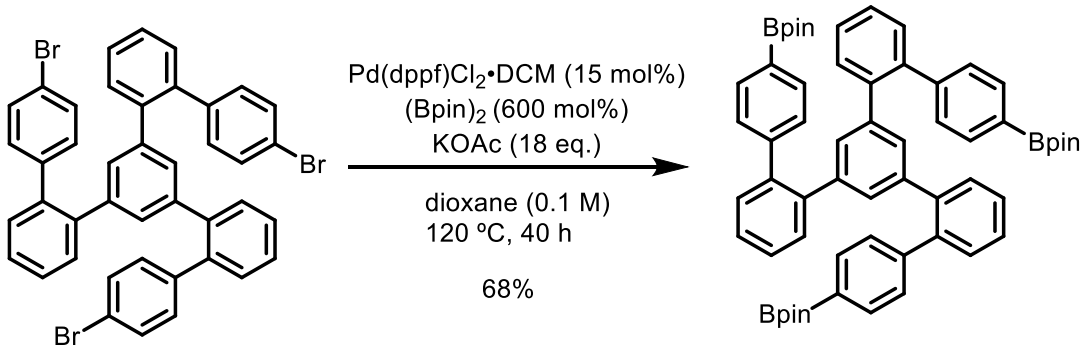
FTIR: (neat): 1739, 1366, 1229, 1217 cm^{-1}.


1.04
6.69
2.90
6.00
1.00
2.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


151.68
142.47
142.06
135.23
134.50
130.36
128.12
123.99
117.48
116.80
27.18
26.80
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23.88
50
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
f1 (ppm)

Preparation of tris-boronic acid pinacol ester **8.7** from tris-bromide **S8.2**:



S8.2 **8.7**

Tris-bromide **S8.2** was synthesized according to known procedures.[15]

To a solution of **S8.2** (2.5 g, 3.2 mmol, 100 mol%), bis(pinacolato)diboron (4.9 g, 19.4 mmol, 600 mol%), and potassium acetate (5.7 g, 58.3 mmol, 18.0 eq.) in dioxane (32.4 mL) was added $Pd(dppf)Cl_2•CH_2Cl_2$ (356 mg, 0.49 mmol, 15 mol%). The mixture was then heated at 120 ˚C for 40 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with DCM (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure with silica gel which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 90:10 to 80:20) to furnish the pale yellow solid. The solid was further purified by recrystallization in $CHCl_3$/hexanes, which provided the title compound **8.7** (2.0 g, 2.2 mmol) in 68% yield as a white solid.

TLC (SiO_2): R_f = 0.49 (hexanes : ethylacetate = 80:20).

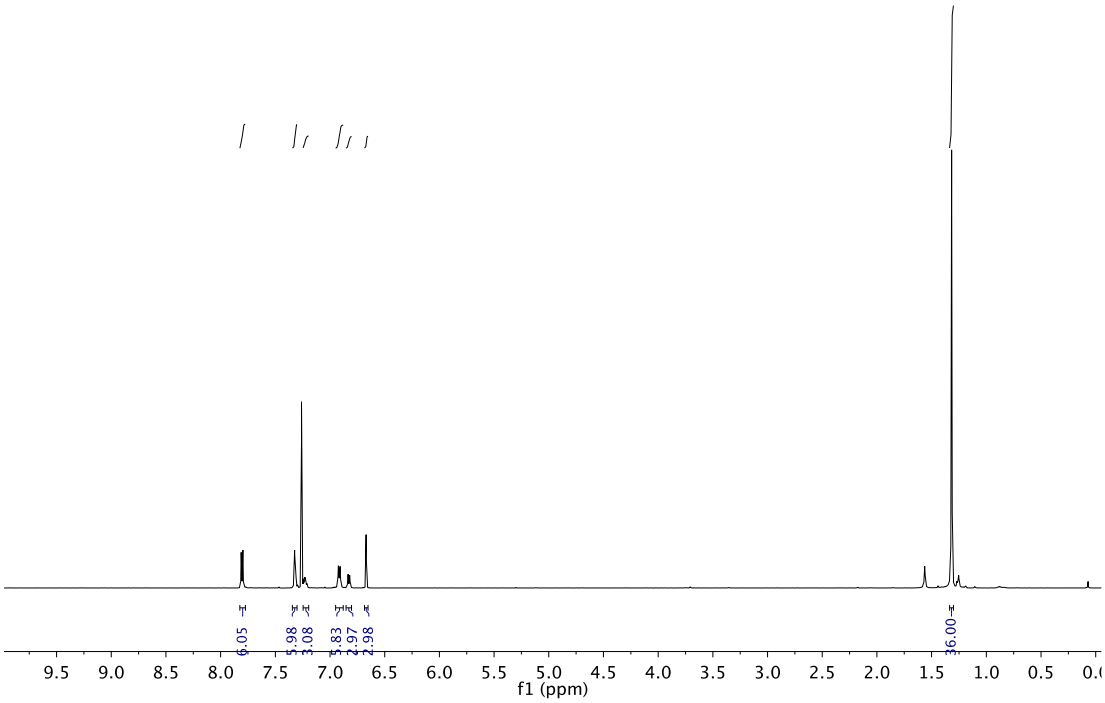
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.9 Hz, 6H), 7.34-7.30 (m, 6H), 7.25-7.20 (m, 3H), 7.36–7.28 (m, 4H), 6.92 (d, *J* = 7.5 Hz, 6H), 6.83 (d, *J* = 7.6 Hz, 3H), 6.67 (s, 3H), 1.32 (s, 36H) ppm.

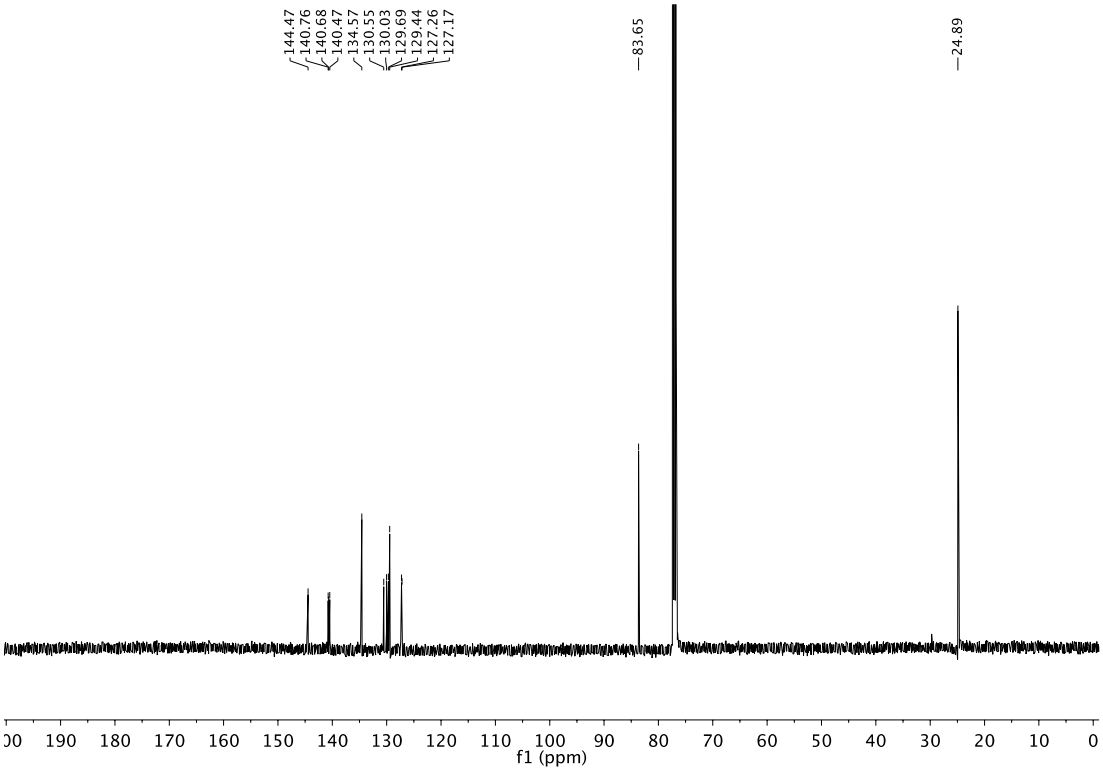
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 144.5, 140.8. 140.7, 140.5, 134.6, 130.6, 130.0, 129.7. 129.4, 127.3, 127.2, 83.7, 24.9 ppm.

MP: 248-253 °C.

HRMS: (ESI) Calculated for $C_{60}H_{63}B_3O_6$ $[M+K]^+$ =951.4562, Found 951.4584.

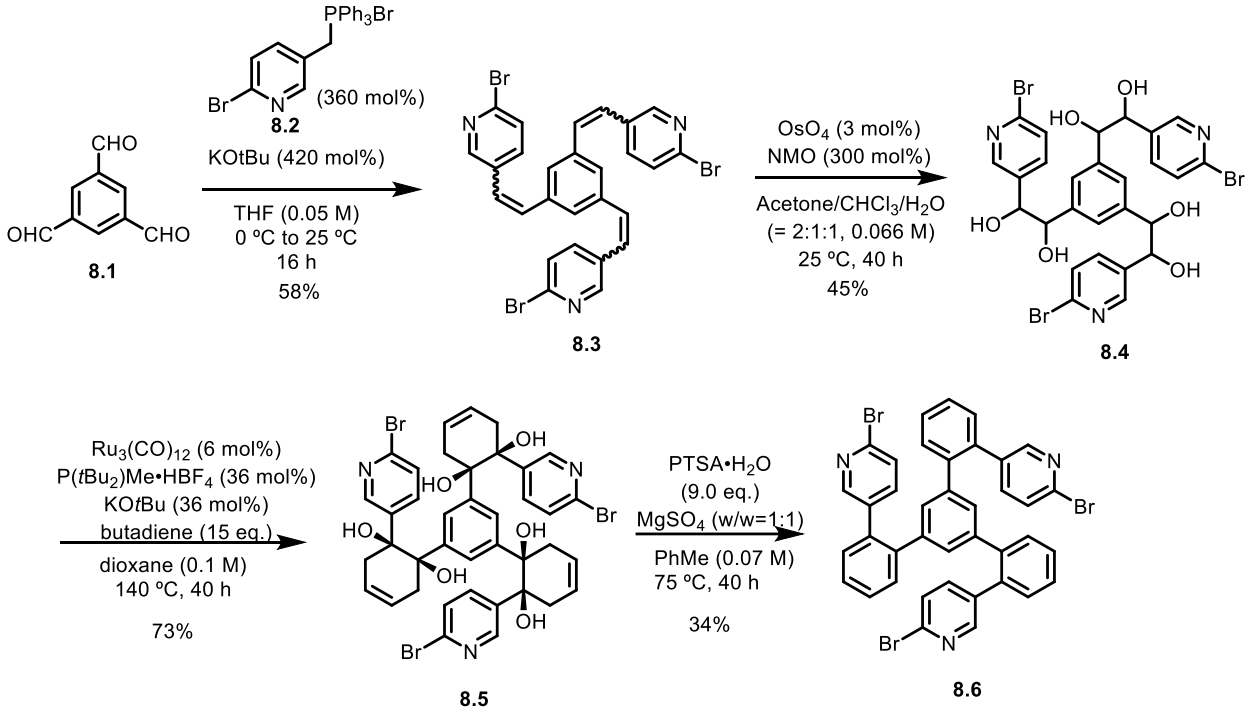
FTIR: (neat): 2976, 1357, 1215, 1091 cm^{-1}.


6.05
5.98
3.08
2.97
2.98
36.00
f1 (ppm)


144.47
140.76
140.68
140.47
134.57
130.55
130.03
129.69
129.44
127.26
127.17
83.65
24.89
f1 (ppm)

Synthesis of *Tris*-bromide

Synthesis of *tris*-bromide **8.6**



Synthesis of triene **8.3** from 1,3,5-tricarbaldehyde **8.1**:

To a solution of KO*t*-Bu (4.72 g, 42.0 mmol, 420 mol%) in anhydrous THF (420 mL) cooled to 0 ˚C was added triphenylphosphonium bromide **8.2** (18.5 g, 36.0 mmol, 360 mol%). The mixture was allowed to stir at the same temperature for 30 min followed by the addition of 1,3,5-tricarbaldehyde **8.1** (1.62 g, 10.0 mmol, 100 mol%) in THF (420 mL) dropwise over 30 min. The reaction was then warmed to room temperature and allowed to stir for 16 hours. The solution was concentrated under vacuum followed by addition of water (50 mL). The aqueous layer was then extracted with Et_2O (3 x 25 mL) and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure provided an oily residue which

was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 90:10 to 80:20) to furnish the title compound **8.3** (3.63 g, 5.8 mmol) in 58% yield as a white solid.

TLC (SiO_2): R_f = 0.39 (hexanes : ethyl acetate = 70:30).

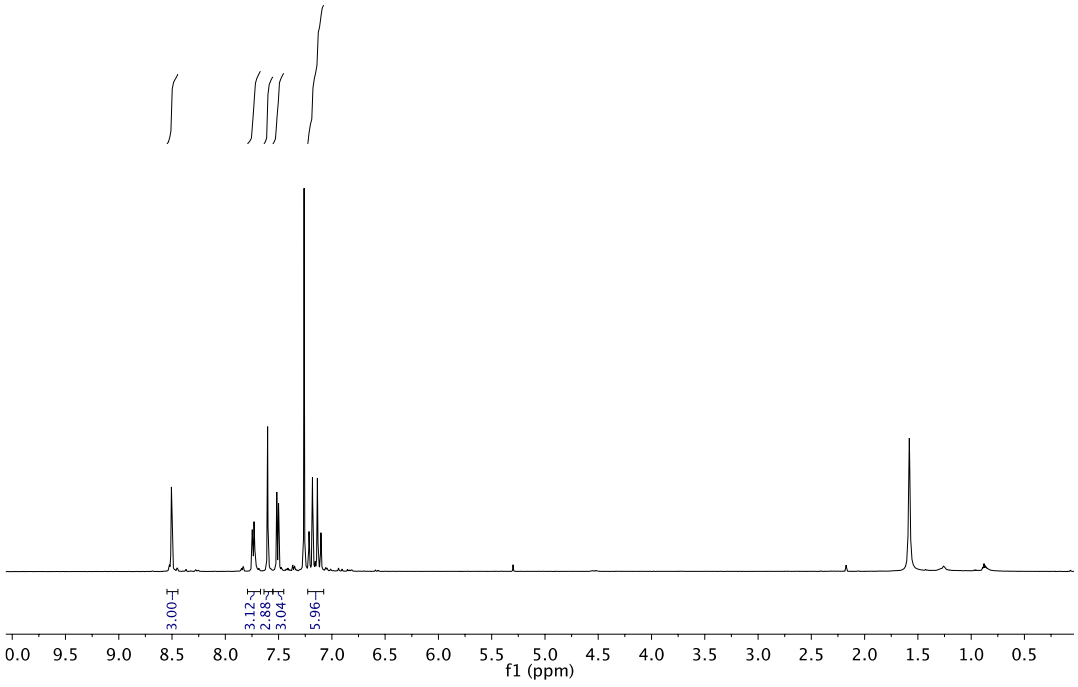
^{1}H NMR: (500 MHz, $CDCl_3$, diastereomer mixtures, (*Z*,*Z*,*Z*)-triene is major): δ = 8.51 (s, 3H), 7.74 (dd, *J* = 8.3, 2.6 Hz, 3H), 7.61 (s, 3H), 7.51 (d, 3H), 7.23-7.09 (m, 6H) ppm.

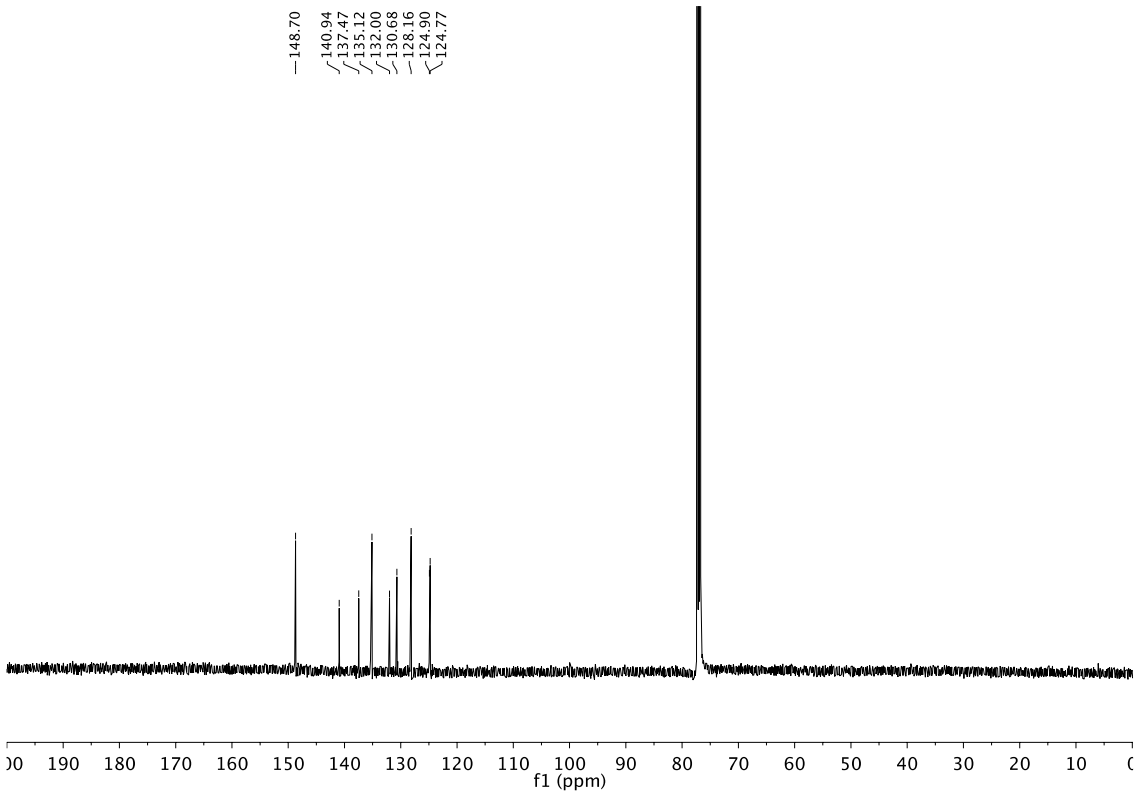
^{13}C NMR: (125 MHz, $CDCl_3$, (*Z*,*Z*,*Z*)-triene): δ = 148.7, 140.9, 137.5, 135.1, 132.0, 130.7, 128.2, 124.9, 124.8 ppm.

MP: decomposed at ~260 ˚C.

HRMS: (ESI) Calculated for $C_{27}H_{18}Br_3N_3$ [M+H$^+$] = 623.9104, Found 623.9116.

FTIR: (neat): 1571, 1547, 1455, 1083 cm^{-1}.


3.00
3.12
2.88
3.04
5.96
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


148.70
140.94
137.47
135.12
132.00
130.68
128.16
124.90
124.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Synthesis of *tris*-diol **8.4** from triene **8.3**:

To a solution of triene **8.3** (3.63 g, 5.0 mmol, 100 mol%) in acetone (38 mL), chloroform (19 mL), and water (18 mL) was added NMO in water (w/w 50%) (3.51 g, 15.0 mmol, 300 mol%). Then, OsO_4 (1.0 M in *t*-BuOH, 0.15 mL, 0.15 mmol, 3 mol%) was added. The mixture was allowed to stir for 40 hours. Toluene (30 mL) and silica gel was added, and concentrated under vacuum. Recovered solid was subjected to flash column chromatography (SiO_2; ethyl acetate = 100 to ethyl acetate:methanol 85:15) to furnish the title compound **8.4** (1.63 g, 2.3 mmol) in 45% yield as a slightly yellow solid. The material was characterized by ^{1}H NMR only.

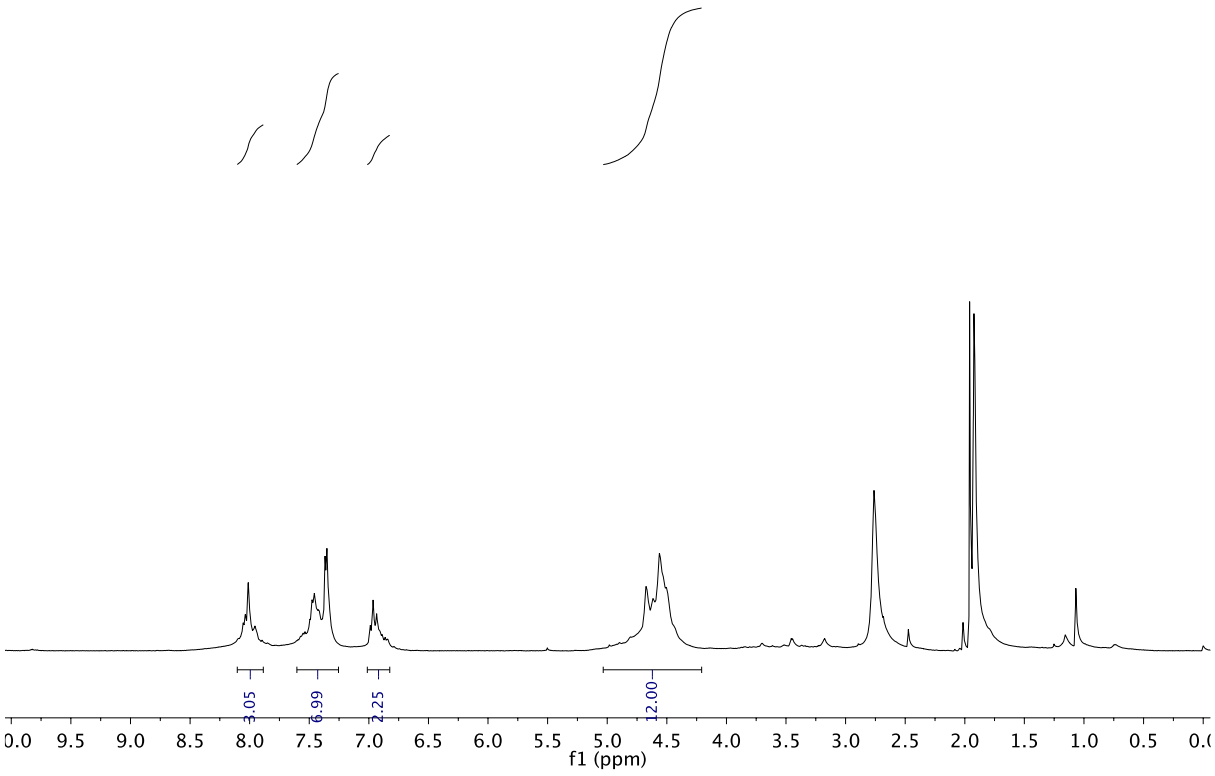
TLC (SiO_2): R_f = 0.32 (ethyl acetate : MeOH = 90:10).

^{1}H NMR: (500 MHz, d_6-acetone, mixture of diastereomers): δ = 8.10–7.87 (m, 3H), 7.60-7.26 (m, 7H), 7.01-6.82 (m, 2H), 5.04-4.20 (m, 12H) ppm.

MP: decomposed at ~160 °C.

HRMS: (ESI) Calculated for $C_{27}H_{24}Br_3N_3O_6$ [M+Na^+] =749.9071, Found 749.9069.

FTIR: (neat): 3294, 1582, 1086 cm^{-1}.


3.05
6.99
2.25
12.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Synthesis of cycloadduct **8.5** from **8.4** by ruthenium catalyzed cycloaddition reactions

A resealable pressure tube (ca. 13 x 100 mm) was charged with $Ru_3(CO)_{12}$ (7.7 mg, 0.017 mmol, 6 mol%), $P(tBu_2)Me{\bullet}HBF_4$ (17.9 mg, 0.072 mmol, 36 mol%), KO*t*Bu (8.1 mg, 0.072 mmol, 36 mol%), *tris*-diol **8.4** (145.2 mg, 0.20 mmol, 100 mol%). The pressure tube was purged with argon and dioxane (2.0 mL) was added via syringe, followed by freshly condensed butadiene (0.26 mL, 3.0 mmol, 15.0 eq). The septum was replaced with a screw cap, and the reaction was placed in a 140 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, hexanes:ethyl acetate =50:50 to ethyl acetate = 100) providing the title compound **8.5** (128.9 mg, 0.15 mmol) in 81% yield as a slightly yellow solid. The material was characterized by ^{1}H NMR only.

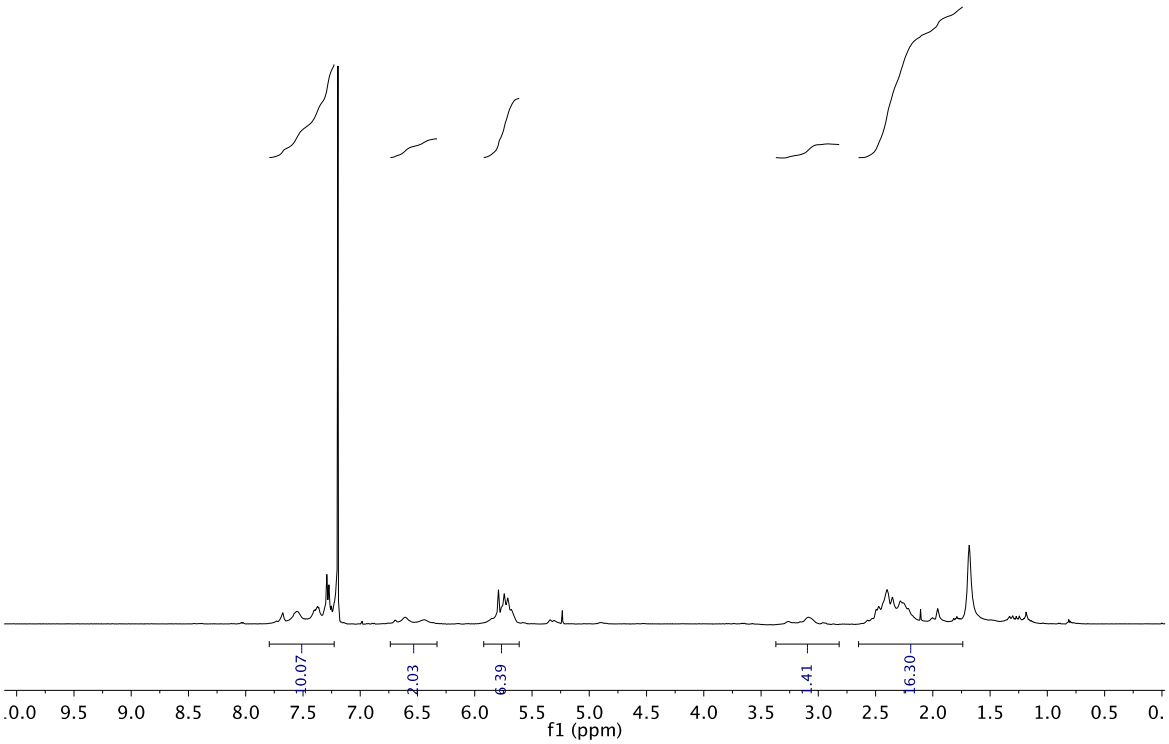
TLC (SiO_2): R_f = 0.34 (hexanes : ethyl acetate = 20:80).

^{1}H NMR: (500 MHz, $CDCl_3$: mixture of diastereomers): δ = 7.86-7.29 (m, 10H), 6.81–6.39 (m, 2H), 5.99-5.67 (m, 6H), 3.44-1.81 (m, 18H) ppm.

MP: decomposed at ~170 ˚C.

HRMS: (ESI) Calculated for $C_{39}H_{36}Br_3N_3O_6$ $[M+H^+]$ =884.0194, Found884.0173.

FTIR: (neat): 3384, 1454, 1085 cm^{-1}.


10.07
2.03
6.39
1.41
16.30
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

Synthesis of tribromide **8.6** by dehydration of **8.5**

A resealable pressure tube (ca. 13 x 100 mm) was charged with cycloadduct **8.5** (100 mg, 0.11 mmol, 100 mol%) followed by *p*-toluenesulfonic acid monohydrate (188.3 mg, 0.99 mmol, 9.0 eq.) and $MgSO_4$ (100 mg, w/w = 1:1 to cycloadduct **8.5**). The pressure tube was purged with argon and toluene (1.6 mL) was added via syringe. The septum was replaced with a screw cap, and the reaction was placed in a 75 ˚C oil bath. After 40 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The toluene was removed *in vacuo*, and the residue was subjected to flash column chromatography (SiO_2, hexanes:ethyl acetate = 90:10 to 80:20) providing the title compound **8.6** (29.0 mg, 0.037 mmol) in 34% yield as a white solid.

TLC (SiO_2): R_f = 0.26 (hexanes : ethylacetate = 80:20).

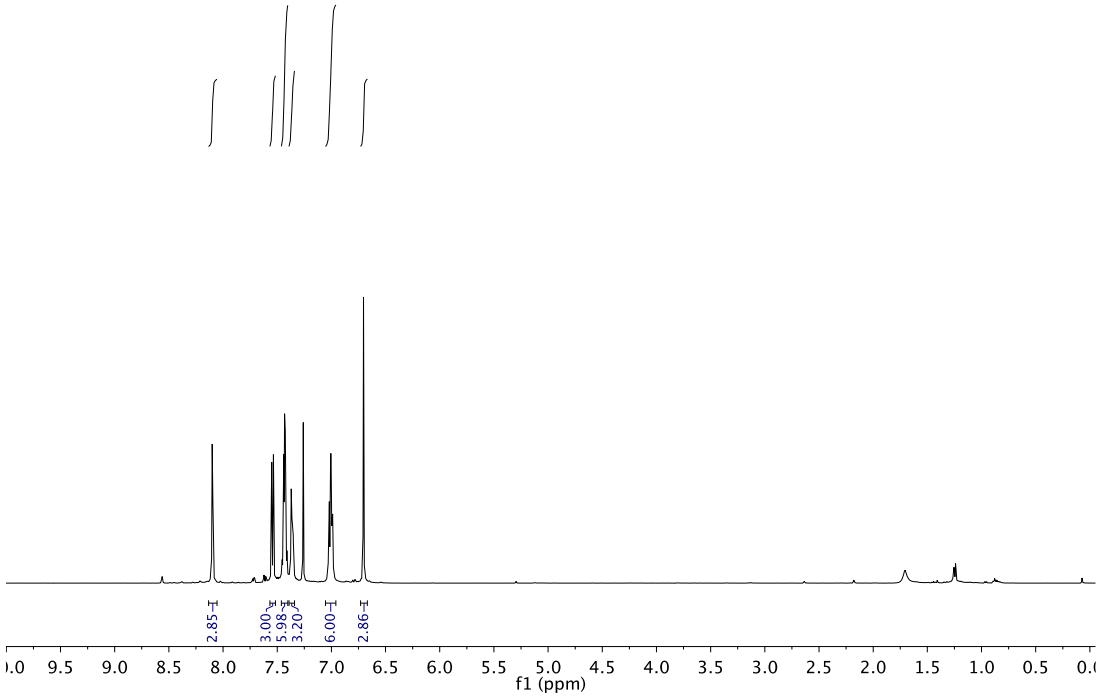
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.5 Hz, 3H), 7.54 (d, 3H), 7.46-7.40 (m, 6H), 7.39-7.34 (m, 3H), 7.05-6.96 (m, 6H), 6.70 (s, 3H) ppm.

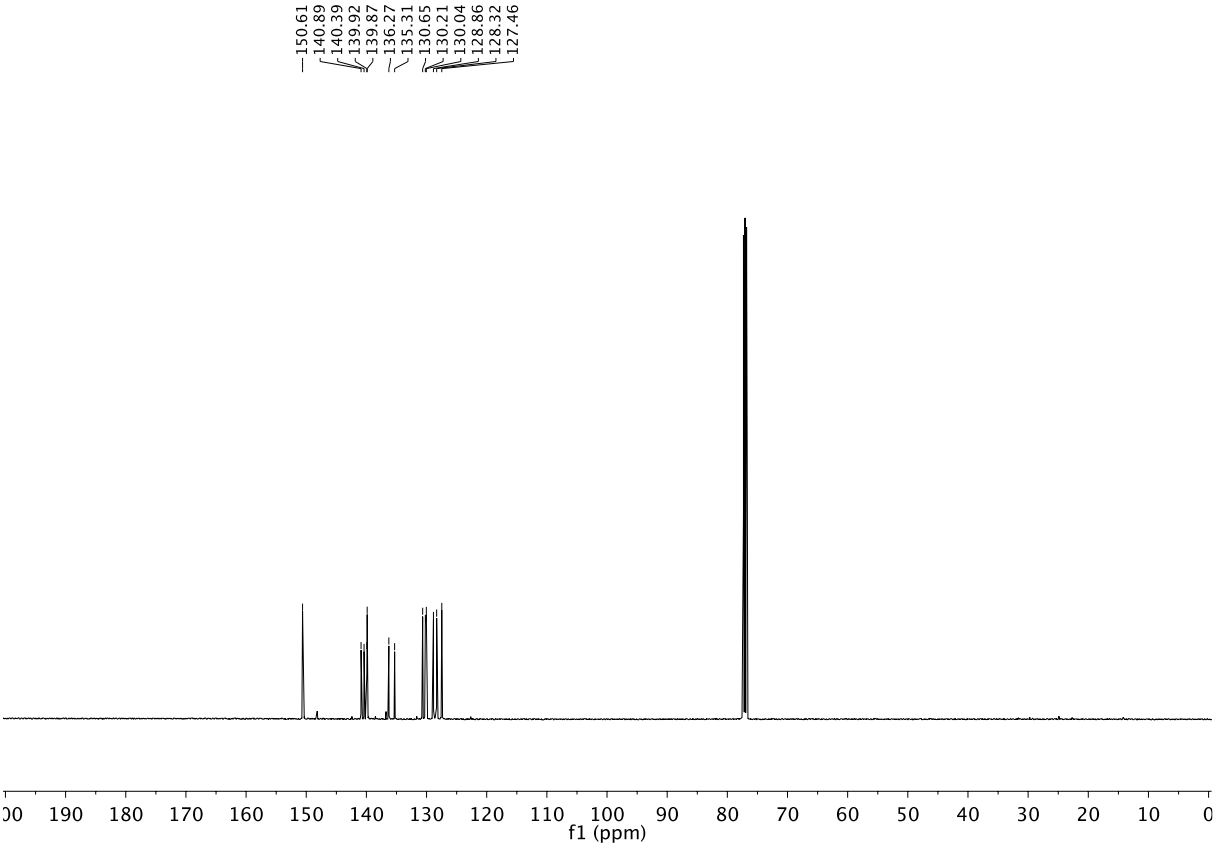
^{13}C NMR: (125 MHz, $CDCl_3$): δ = 150.6, 140.9, 140.4, 139.9, 139.9, 136.3, 135.3, 130.7, 130.2, 130.0, 128.9, 128.3, 127.5 ppm.

MP: decomposed at ~200 °C.

HRMS: (ESI) Calculated for $C_{39}H_{24}Br_3N_6$ $[M+H^+]$ =775.9560, Found775.9543.

FTIR: (neat): 1357, 1091, 760 cm^{-1}.


2.85
3.00
5.98
3.20
6.00
2.86
f1 (ppm)


150.61
140.89
140.39
139.92
139.87
136.27
135.31
130.65
130.21
130.04
128.86
128.32
127.46
f1 (ppm)

Synthesis of Helical Rod-Like N-Doped Cages

Synthesis of small phenylene cage **8.8**

A resealable pressure tube was charged with *tris*-bromide **8.6** (20.0 mg, 0.026 mmol, 100 mol%), *tris*-boronic acid pinacol ester **8.7** (23.6 mg, 0.0026 mmol, 100 mol%), $Pd(PPh_3)Cl_2$ (3.6 mg, 5.2 µmol, 20 mol%) and potassium carbonate (71.4 mg, 0.52 mmol, 20.0 eq.) in dioxane (0.83 mL) and water (0.21 mL). The mixture was then heated at 120 ˚C. After 40 h stirring, ethylenediaminetetraacetic acid (EDTA) in NaOH aqueous solution was added. The aqueous layer was then extracted with $CHCl_3$ (3 x 20 mL) and the combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and filtered. Evaporation under reduced pressure with silica gel which was subjected to flash column chromatography (SiO_2; hexanes:ethyl acetate = 95:5 to 80:20) to furnish the pale yellow solid. The solid was further purified by recrystallization in $CHCl_3$/hexanes, which provided the title compound **8.8** (5.2 mg, 4.9 µmol) in 19% yield as a white solid.

TLC (SiO_2): R_f = 0.35 (hexanes : EtOAc = 70:30).

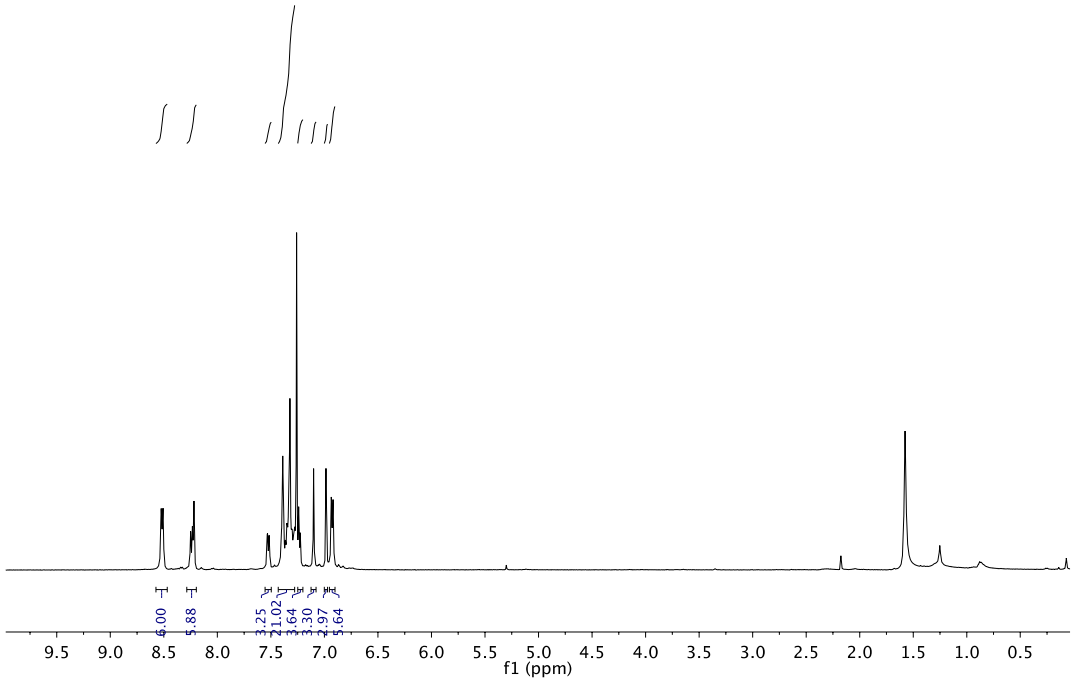
^{1}H NMR: (500 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.1 Hz, 6H), 8.28-8.20 (m, 6H), 7.52 (d, *J* = 8.3 Hz, 3H), 7.43-7.28 (m, 21H), 7.25-7.20 (m, 3H), 7.10 (s, 3H), 6.99 (s, 3H), 6.93 (d, *J* = 8.1 Hz, 3H) ppm.

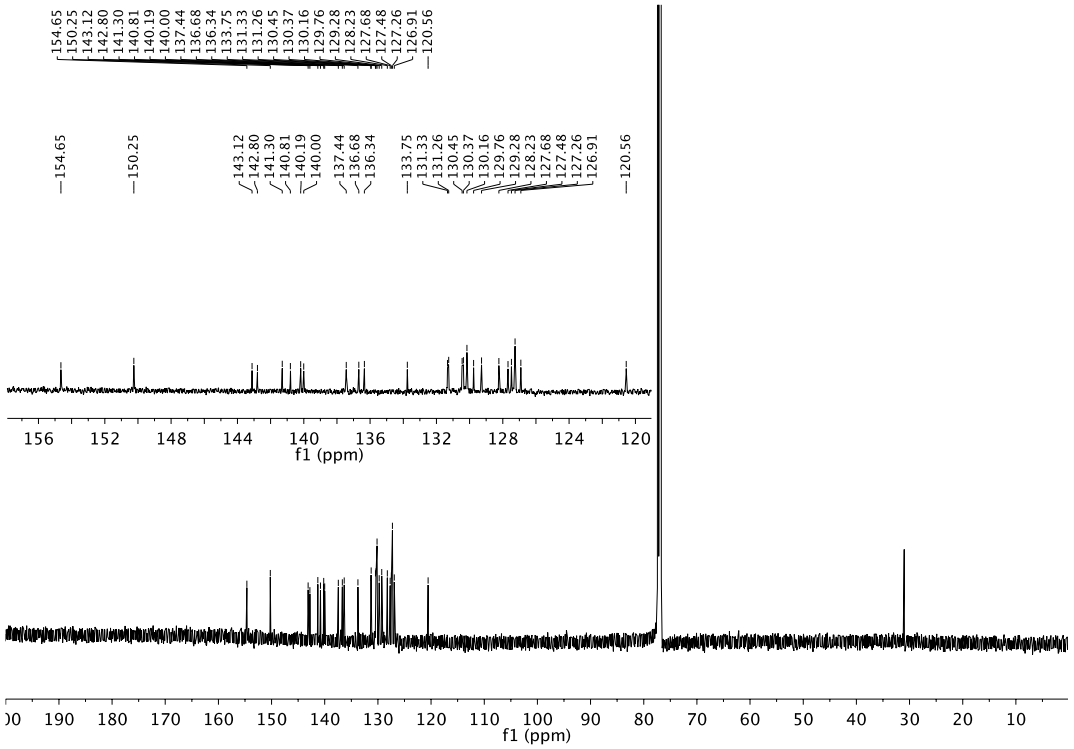
^{13}C NMR: (125 MHz, $CDCl_3$): δ =154.7, 150.3, 143.1, 142.8, 141.3, 140.8, 140.2, 140.0, 137.4, 136.7, 136.3, 133.8, 131.3, 131.3, 130.5, 130.4, 130.2, 129.8, 129.3, 128.2, 127.7, 127.5, 127.3, 126.9, 120.6.

MP: decomposed at ~270 ˚C.

HRMS: (ESI) Calculated for $C_{81}H_{51}N_3$ $[M+H^+]$ = 1066.4156, Found 1066.4154.

FTIR: (neat): 1469, 1356, 758 cm^{-1}.


6.00
5.88
3.25
21.02
3.64
3.30
2.97
5.64
f1 (ppm)


154.65
150.25
143.12
142.80
141.30
140.81
140.19
140.00
137.44
136.68
136.34
133.75
131.33
131.26
130.45
130.37
130.16
129.76
129.28
128.23
127.68
127.48
127.26
126.91
120.56
f1 (ppm)

Synthesis of Ir(III)-N-Cages (8.9)

Synthesis of small phenylene cage **8.9**

A resealable pressure tube was charged with N-cage **8.8** (5.0 mg, 4.7 μmol, 100 mol%) and $Ir(acac)_3$ (2.3 mg, 4.7 μmol, 100 mol%) in ethylene glycol (2.4 mL) and 1,2-dichlorobenzene (2.4 mL). The mixture was then heated at 210 ˚C. After 112 hours, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (SiO_2, hexanes:DCM =30:70 to 50:50) providing the title compound **8.9** (2.6 mg, 2.1 μmol) in 45% yield as a orange solid.

TLC (SiO_2): R_f = 0.33 (hexanes : EtOAc = 70:30).

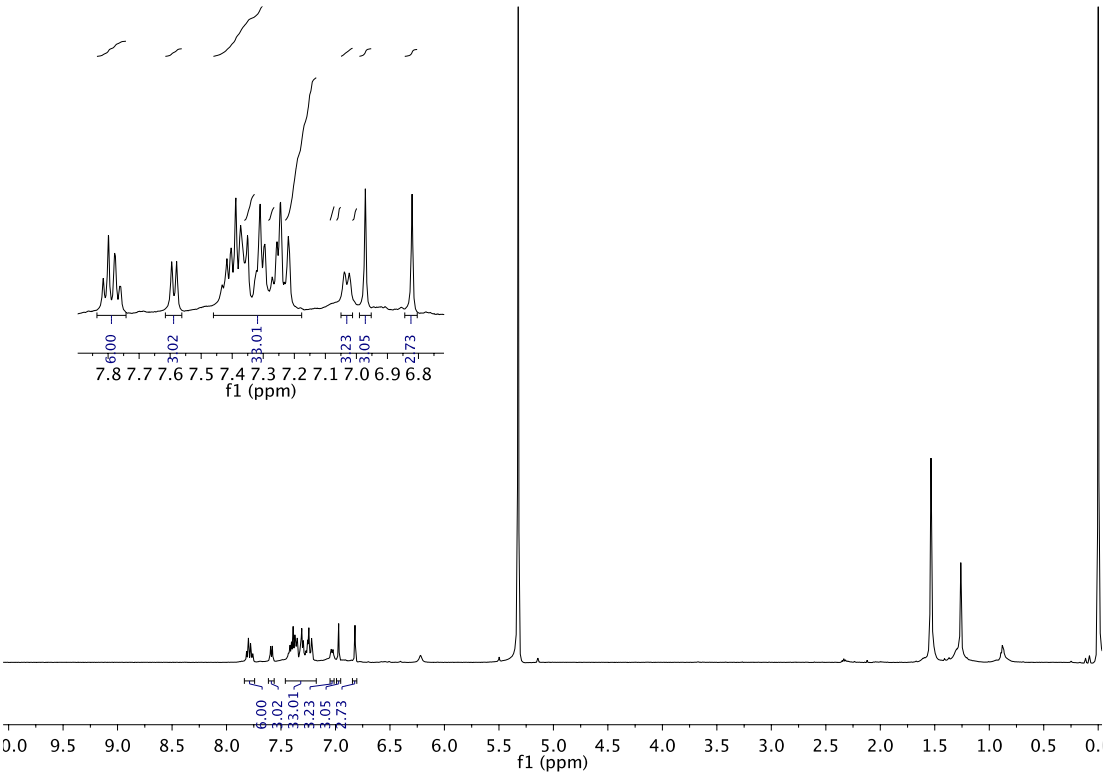
^{1}H NMR: (500 MHz, CD_2Cl_2): δ = 7.70 (d, *J* = 8.0 Hz, 12H), 7.44–7.36 (m, 12H), 7.34–7.25 (m, 12H), 7.15 (d, *J* = 7.9 Hz, 12H) ppm.

^{13}C NMR: (125 MHz, $CDCl_3$): δ = 142.9, 140.6, 139.7, 139.2, 137.7, 131.7, 130.6, 130.4, 129.4, 127.7, 126.9, 126.2.

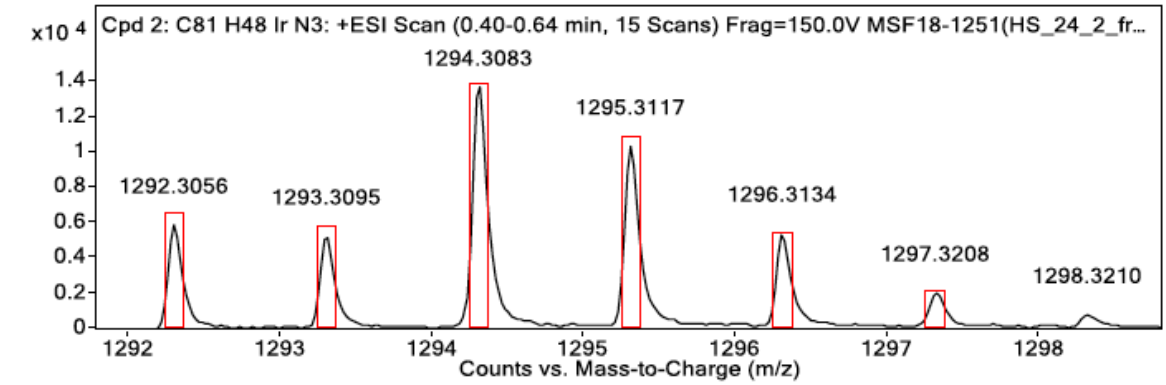
MP: >300 °C.

HRMS: (ESI) Calculated for $C_{81}H_{48}IrN_3$ $[M+K^+]$ = 1294.3083, Found 1294.3115.

FTIR: (neat): 2925, 1457, 1376, 1217 cm^{-1}.



MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
1255.3464			20889			
1292.3056	1292.3086	1	5884	C81H48IrN3	(M+K)+	2.28
1293.3095	1293.3119	1	5246	C81H48IrN3	(M+K)+	1.81
1294.3083	1294.3115	1	13848	C81H48IrN3	(M+K)+	2.48
1295.3117	1295.3143	1	10336	C81H48IrN3	(M+K)+	2.05
1296.3134	1296.3162	1	5410	C81H48IrN3	(M+K)+	2.18
1297.3208	1297.3178	1	2034	C81H48IrN3	(M+K)+	-2.29
1298.3210	1298.3196	1	797	C81H48IrN3	(M+K)+	-1.05
1299.3501	1299.3218	1	447	C81H48IrN3	(M+K)+	-21.8
1300.3597	1300.3243	1	387	C81H48IrN3	(M+K)+	-27.16

--- End Of Report ---

Chiral HPLC-MS Separation of Ir(III)-N-Cage (8.9)

The iridium-based nitrogen phenylene cage (Ir(III)-N-Cage) was separated into its two enantiomers using a Shimadzu triple quadrupole LC–MS instrument, LCMS-8040, (Shimadzu, Tokyo, Japan). All mass spectrometry (MS) was done in the positive ion mode with an electrospray ionization source. The parameters were set as follows: nebulizer gas flow, 3 L/min; drying gas flow, 15 L/min; desolvation line temperature, 250 °C; heat block temperature, 400 °C. Secondary ion monitoring (SIM) was utilized at an *m/z* of 1256.35 (molecular weight of Ir(III)-N-Cage + 1), which is shown below. The separations of Ir(III)-N-Cage by the R-naphthylethyl-derivatized cyclofructan-6 (CF6-RN) and 3,5-dimethylphenyl-derivatized cyclofructan-7 (CF7-DMP) chiral stationary phases are illustrated. Both columns were 150 x 4.6 mm i.d. in dimension and their respective selectors bonded to 5 µm fully porous particles. They were obtained from AZYP, LLC (Arlington, TX, USA). The separation was carried out at room temperature and at 1.0 mL/min using 100% methanol as the mobile phase.

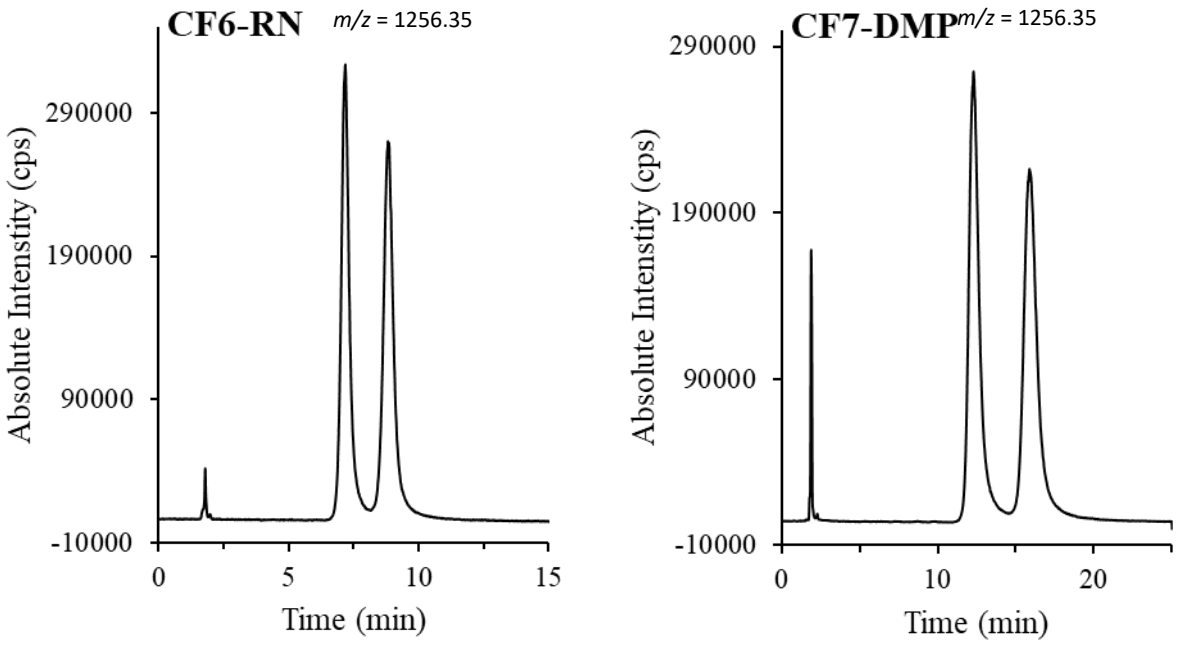


Fig. 8.3 SIM at *m/z* = 1256.35 of the separation of Ir(III)-N-Cage using CF6-RN and CF7-DMPcolumns (150 x 4.6 mm i.d., 5 µm fully porous particles) at 1.0 mL/min of 100% methanol.

Circular Dichroism Chiral Detector Study of Ir(III)-N-Cage

Further confirmation of the enantiomeric separation of Ir(III)-N-Cage was performed using a Jasco CD-2095 (JASCO, Easton, MD, USA) circular dichroism chiral detector (CD). It was utilized with manual injection using a Rheodyne Model 7225 injector and a Shimadzu LC-6A pump. The racemic Ir(III)-N-Cage was separated with the CF6-RN and CF7-DMP columns using 100% methanol at 1.0 mL/min and detection at 320 nm. The figure below shows the UV (in black) and CD (in red) chromatograms of the racemic sample. Enantiomer peaks 1 and 2 are labeled. The elution order of the enantiomers was reversed.

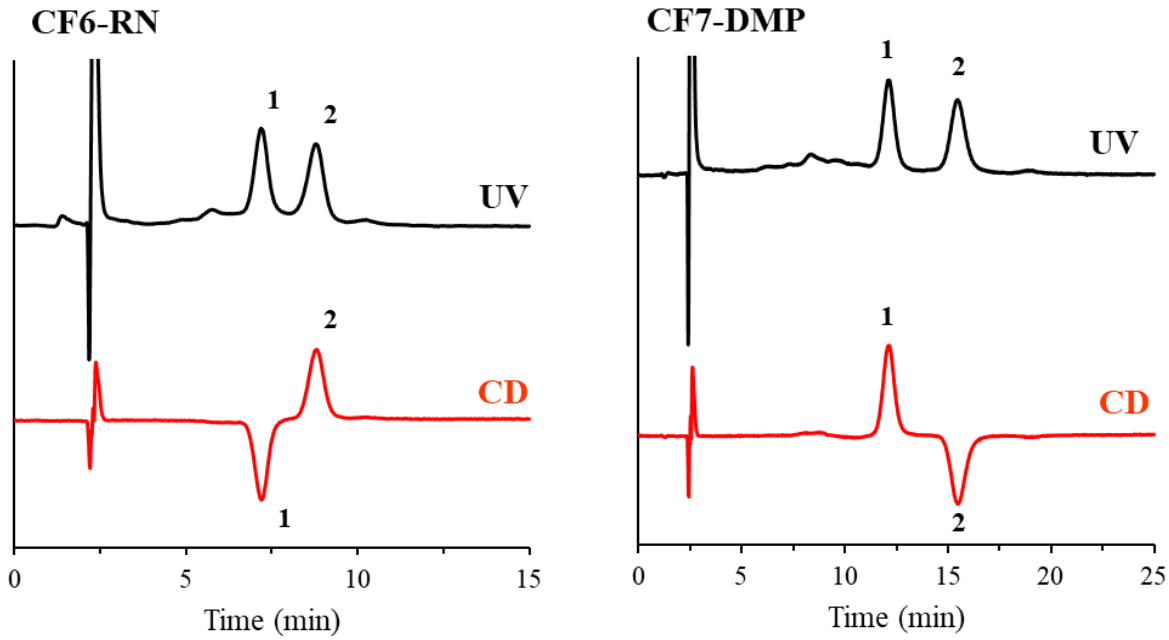


Fig. 8.4. UV and CD chromatograms of the enantiomeric separation of Ir(III)-N-Cage using the method described above with the CF6-RN (left) and CF7-DMP (right) columns at 320 nm.

With another injection the flow was stopped, and a CD spectrum was collected at the top of the first and second chromatographic peaks. The figure below shows the CD spectra of each peak (red corresponds to the first enantiomer peak and blue to the second enantiomer peak).

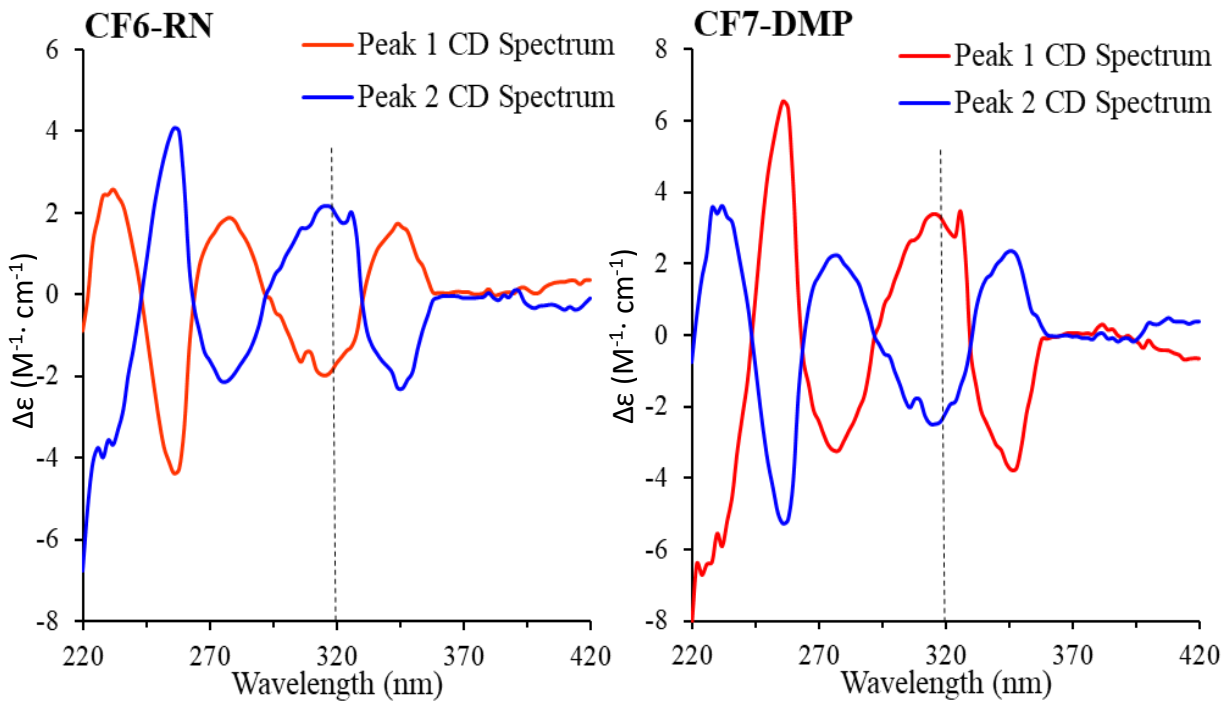


Fig. 8.5. CD spectra of 1st and 2nd chromatographic peaks from the enantiomeric separation of Ir(III)-N-Cage with the CF6-RN (left) and the CF7-DMP (right) columns using the stopped flow method described above. A dotted line was made at 320 nm in reference to the CD chromatograms illustrated above.

Single Crystal Diffraction Data

X-ray Experimental for $C_{81}H_{51}N_3$: Crystals grew as clusters of large, colorless prisms by vapor diffusion of pentane into a DCM solution. The data crystal was cut from a larger crystal and had approximate dimensions; 0.24 x 0.19 x 0.14 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 661 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 17.5 seconds per frame for frames collected with a detector offset of +/- 37.7° and 60 seconds per frame with frames collected with a detector offset of +/- 111.0°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46.[16] The structure was solved by direct methods using SIR2004[17] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[18] Structure analysis was aided by use of the programs PLATON[19] and WinGX.[20] The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). A large solvent void containing what appeared to be pentane was removed from the scattering by the use of the program, SQUEEZE[21], as incorporated into PLATON. The absolute configuration was checked using the method of Flack[22] and confirmed using the Hooft y-parameter method, which resulted in a Hooft y-parameter of 0.05(15).[23]

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.042*P)^2 + (1.6853*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0808, with R(F) equal to 0.0301 and a goodness of fit, S, = 1.01. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[24] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[25] All figures were generated using SHELXTL/PC.[26] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 8.1. Crystal data and structure refinement for **8.8**.

Empirical formula	C81 H51 N3
Formula weight	1066.24
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	cubic
Space group	P 21 3
Unit cell dimensions	a = 23.94490(10) Å □= 90°.
	b = 23.94490(10) Å □= 90°.
	c = 23.94490(10) Å □ = 90°.
Volume	13729.01(17) $Å^3$
Z	8
Density (calculated)	1.032 Mg/m^3
Absorption coefficient	0.457 mm^{-1}
F(000)	4464
Crystal size	0.240 x 0.190 x 0.140 mm^3
Theta range for data collection	2.610 to 73.293°.
Index ranges	-28<=h<=27, -18<=k<=29, -29<=l<=29
Reflections collected	43047
Independent reflections	9037 [R(int) = 0.0257]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.570
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9037 / 0 / 505
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0780
R indices (all data)	R1 = 0.0335, wR2 = 0.0808
Absolute structure parameter	0.05(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.103 and -0.122 $e.Å^{-3}$

Table 8.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8.8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	-536(1)	6675(1)	9556(1)	34(1)
C2	-1014(1)	7010(1)	9552(1)	39(1)
C3	-1544(1)	6778(1)	9526(1)	43(1)
C4	-1605(1)	6202(1)	9506(1)	41(1)
C5	-1139(1)	5864(1)	9532(1)	36(1)
C6	-601(1)	6093(1)	9559(1)	32(1)
C7	-121(1)	5702(1)	9615(1)	31(1)
C8	-51(1)	5259(1)	9242(1)	30(1)
C9	18(1)	6952(1)	9492(1)	33(1)
C10	396(1)	6768(1)	9088(1)	36(1)
C11	1021(1)	7498(1)	9257(1)	33(1)
C12	670(1)	7700(1)	9671(1)	36(1)
C13	170(1)	7434(1)	9785(1)	37(1)
C14	1562(1)	7758(1)	9097(1)	33(1)
C15	1716(1)	8302(1)	9246(1)	40(1)
C16	2229(1)	8522(1)	9085(1)	40(1)
C17	2601(1)	8212(1)	8762(1)	35(1)
C18	2438(1)	7670(1)	8616(1)	35(1)
C19	1935(1)	7448(1)	8784(1)	33(1)
C20	3169(1)	8428(1)	8616(1)	36(1)
C21	3470(1)	8715(1)	9025(1)	45(1)
C22	4013(1)	8895(1)	8930(1)	49(1)
C23	4268(1)	8790(1)	8431(1)	44(1)
C24	3976(1)	8507(1)	8014(1)	39(1)
C25	3426(1)	8332(1)	8098(1)	33(1)
C26	3127(1)	8079(1)	7611(1)	30(1)
C27	2652(1)	8337(1)	7394(1)	31(1)
C28	1653(1)	6953(1)	11154(1)	33(1)
C29	1136(1)	6879(1)	10889(1)	36(1)
C30	643(1)	6871(1)	11186(1)	39(1)

C31	651(1)	6923(1)	11763(1)	40(1)
C32	1157(1)	7007(1)	12033(1)	37(1)
C33	1658(1)	7034(1)	11738(1)	33(1)
C34	2174(1)	7189(1)	12051(1)	32(1)
C35	2340(1)	6890(1)	12519(1)	32(1)
C36	2174(1)	6912(1)	10817(1)	33(1)
C37	2636(1)	6614(1)	11014(1)	33(1)
C38	3133(1)	6725(1)	10186(1)	33(1)
C39	2696(1)	7032(1)	9965(1)	37(1)
C40	2216(1)	7123(1)	10278(1)	37(1)
C41	3664(1)	6604(1)	9884(1)	35(1)
C42	3733(1)	6688(1)	9311(1)	40(1)
C43	4240(1)	6568(1)	9057(1)	42(1)
C44	4690(1)	6361(1)	9362(1)	37(1)
C45	4612(1)	6286(1)	9934(1)	37(1)
C46	4112(1)	6409(1)	10188(1)	34(1)
C47	5253(1)	6266(1)	9111(1)	41(1)
C48	5483(1)	6673(1)	8764(1)	50(1)
C49	6023(1)	6632(1)	8566(1)	61(1)
C50	6352(1)	6185(1)	8718(1)	62(1)
C51	6132(1)	5772(1)	9053(1)	52(1)
C52	5582(1)	5799(1)	9245(1)	41(1)
C53	5359(1)	5311(1)	9560(1)	37(1)
C54	5633(1)	5114(1)	10032(1)	38(1)
N1	881(1)	7029(1)	8970(1)	38(1)
N2	3098(1)	6520(1)	10715(1)	37(1)

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Table 8.3. Bond lengths [Å] and angles [°] for **8.8**.

C1-C2	1.398(3)	C18-C19	1.376(3)
C1-C6	1.404(3)	C18-H18	0.95
C1-C9	1.490(3)	C19-H19	0.95
C2-C3	1.386(3)	C20-C21	1.397(3)
C2-H2	0.95	C20-C25	1.405(3)
C3-C4	1.388(3)	C21-C22	1.389(3)
C3-H3	0.95	C21-H21	0.95
C4-C5	1.379(3)	C22-C23	1.363(3)
C4-H4	0.95	C22-H47A	0.95
C5-C6	1.400(3)	C23-C24	1.395(3)
C5-H5	0.95	C23-H23	0.95
C6-C7	1.489(2)	C24-C25	1.396(3)
C7-C8#1	1.390(3)	C24-H24	0.95
C7-C8	1.398(3)	C25-C26	1.497(2)
C8-H8	0.95	C26-C27#1	1.390(2)
C9-C10	1.397(3)	C26-C27	1.394(2)
C9-C13	1.398(3)	C27-H27	0.95
C10-N1	1.347(3)	C28-C29	1.402(3)
C10-H10	0.95	C28-C33	1.412(3)
C11-N1	1.358(2)	C28-C36	1.489(3)
C11-C12	1.386(3)	C29-C30	1.378(3)
C11-C14	1.489(3)	C29-H29	0.95
C12-C13	1.384(3)	C30-C31	1.387(3)
C12-H12	0.95	C30-H30	0.95
C13-H13	0.95	C31-C32	1.388(3)
C14-C19	1.383(3)	C31-H31	0.95
C14-C15	1.399(3)	C32-C33	1.395(3)
C15-C16	1.392(3)	C32-H23A	0.95
C15-H15	0.95	C33-C34	1.493(2)
C16-C17	1.394(3)	C34-C35	1.389(3)
C16-H16	0.95	C34-C35#2	1.400(3)
C17-C18	1.400(3)	C35-H35	0.95
C17-C20	1.496(3)	C36-C40	1.390(3)

C36-C37	1.398(3)	C45-C46	1.377(3)
C37-N2	1.339(2)	C45-H45	0.95
C37-H37	0.95	C46-H46	0.95
C38-N2	1.360(2)	C47-C48	1.395(3)
C38-C39	1.382(3)	C47-C52	1.404(3)
C38-C41	1.492(3)	C48-C49	1.380(3)
C39-C40	1.390(3)	C48-H48	0.95
C39-H39	0.95	C49-C50	1.378(4)
C40-H40	0.95	C49-H49	0.95
C41-C46	1.378(3)	C50-C51	1.378(3)
C41-C42	1.396(3)	C50-H50	0.95
C42-C43	1.387(3)	C51-C52	1.397(3)
C42-H42	0.95	C51-H51	0.95
C43-C44	1.394(3)	C52-C53	1.490(3)
C43-H43	0.95	C53-C54	1.388(3)
C44-C45	1.394(3)	C53-C54#3	1.396(3)
C44-C47	1.494(3)	C54-H54	0.95

C2-C1-C6	118.49(18)	C1-C6-C7	122.54(17)
C2-C1-C9	118.32(17)	C8#1-C7-C8	118.34(17)
C6-C1-C9	122.84(17)	C8#1-C7-C6	120.84(16)
C3-C2-C1	121.44(19)	C8-C7-C6	120.78(16)
C3-C2-H2	119.3	C7#4-C8-C7	121.66(18)
C1-C2-H2	119.3	C7#4-C8-H8	119.2
C2-C3-C4	119.67(19)	C7-C8-H8	119.2
C2-C3-H3	120.2	C10-C9-C13	116.00(18)
C4-C3-H3	120.2	C10-C9-C1	120.52(17)
C5-C4-C3	119.78(19)	C13-C9-C1	123.20(17)
C5-C4-H4	120.1	N1-C10-C9	123.91(18)
C3-C4-H4	120.1	N1-C10-H10	118.0
C4-C5-C6	121.05(18)	C9-C10-H10	118.0
C4-C5-H5	119.5	N1-C11-C12	120.04(18)
C6-C5-H5	119.5	N1-C11-C14	115.52(17)
C5-C6-C1	119.45(17)	C12-C11-C14	124.43(17)
C5-C6-C7	117.95(16)	C13-C12-C11	120.34(18)

C13-C12-H12	119.8	C23-C24-C25	121.01(19)
C11-C12-H12	119.8	C23-C24-H24	119.5
C12-C13-C9	120.40(18)	C25-C24-H24	119.5
C12-C13-H13	119.8	C24-C25-C20	119.44(17)
C9-C13-H13	119.8	C24-C25-C26	117.49(17)
C19-C14-C15	117.93(18)	C20-C25-C26	122.94(17)
C19-C14-C11	118.49(17)	C27#1-C26-C27	119.23(18)
C15-C14-C11	123.58(18)	C27#1-C26-C25	120.51(16)
C16-C15-C14	120.92(19)	C27-C26-C25	120.14(16)
C16-C15-H15	119.5	C26#4-C27-C26	120.77(18)
C14-C15-H15	119.5	C26#4-C27-H27	119.6
C15-C16-C17	121.08(19)	C26-C27-H27	119.6
C15-C16-H16	119.5	C29-C28-C33	118.23(18)
C17-C16-H16	119.5	C29-C28-C36	119.11(17)
C16-C17-C18	117.05(18)	C33-C28-C36	122.57(17)
C16-C17-C20	121.73(18)	C30-C29-C28	121.56(18)
C18-C17-C20	121.04(18)	C30-C29-H29	119.2
C19-C18-C17	121.89(18)	C28-C29-H29	119.2
C19-C18-H18	119.1	C29-C30-C31	120.17(18)
C17-C18-H18	119.1	C29-C30-H30	119.9
C18-C19-C14	121.12(18)	C31-C30-H30	119.9
C18-C19-H19	119.4	C30-C31-C32	119.25(19)
C14-C19-H19	119.4	C30-C31-H31	120.4
C21-C20-C25	118.21(18)	C32-C31-H31	120.4
C21-C20-C17	118.37(18)	C31-C32-C33	121.40(18)
C25-C20-C17	123.32(17)	C31-C32-H23A	119.3
C22-C21-C20	121.5(2)	C33-C32-H23A	119.3
C22-C21-H21	119.3	C32-C33-C28	119.28(17)
C20-C21-H21	119.3	C32-C33-C34	117.96(17)
C23-C22-C21	120.3(2)	C28-C33-C34	122.60(17)
C23-C22-H47A	119.9	C35-C34-C35#2	119.29(18)
C21-C22-H47A	119.9	C35-C34-C33	120.79(17)
C22-C23-C24	119.5(2)	C35#2-C34-C33	119.83(16)
C22-C23-H23	120.2	C34-C35-C34#3	120.71(18)
C24-C23-H23	120.2	C34-C35-H35	119.6

C34#3-C35-H35	119.6	C44-C45-H45	119.3
C40-C36-C37	116.26(18)	C45-C46-C41	121.14(18)
C40-C36-C28	122.69(17)	C45-C46-H46	119.4
C37-C36-C28	120.84(17)	C41-C46-H46	119.4
N2-C37-C36	123.93(17)	C48-C47-C52	118.1(2)
N2-C37-H37	118.0	C48-C47-C44	119.3(2)
C36-C37-H37	118.0	C52-C47-C44	122.39(18)
N2-C38-C39	120.13(18)	C49-C48-C47	121.7(2)
N2-C38-C41	115.71(17)	C49-C48-H48	119.2
C39-C38-C41	124.15(17)	C47-C48-H48	119.2
C38-C39-C40	120.17(18)	C50-C49-C48	120.0(2)
C38-C39-H39	119.9	C50-C49-H49	120.0
C40-C39-H39	119.9	C48-C49-H49	120.0
C36-C40-C39	120.23(18)	C51-C50-C49	119.5(2)
C36-C40-H40	119.9	C51-C50-H50	120.3
C39-C40-H40	119.9	C49-C50-H50	120.3
C46-C41-C42	118.43(18)	C50-C51-C52	121.3(2)
C46-C41-C38	118.20(17)	C50-C51-H51	119.4
C42-C41-C38	123.36(18)	C52-C51-H51	119.4
C43-C42-C41	120.34(19)	C51-C52-C47	119.4(2)
C43-C42-H42	119.8	C51-C52-C53	117.9(2)
C41-C42-H42	119.8	C47-C52-C53	122.57(18)
C42-C43-C44	121.30(18)	C54-C53-C54#3	119.4(2)
C42-C43-H43	119.3	C54-C53-C52	120.59(19)
C44-C43-H43	119.3	C54#3-C53-C52	119.93(18)
C45-C44-C43	117.33(19)	C53-C54-C53#2	120.6(2)
C45-C44-C47	119.71(19)	C53-C54-H54	119.7
C43-C44-C47	122.74(18)	C53#2-C54-H54	119.7
C46-C45-C44	121.44(19)	C10-N1-C11	119.28(17)
C46-C45-H45	119.3	C37-N2-C38	119.27(17)

Symmetry transformations used to generate equivalent atoms:

#1 y-1/2,-z+3/2,-x+1 #2 -z+3/2,-x+1,y+1/2 #3 -y+1,z-1/2,-x+3/2

#4 -z+1,x+1/2,-y+3/2

Table 8.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8.8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	37(1)	37(1)	27(1)	4(1)	2(1)	4(1)
C2	41(1)	38(1)	38(1)	2(1)	0(1)	7(1)
C3	38(1)	49(1)	41(1)	1(1)	1(1)	14(1)
C4	32(1)	53(1)	36(1)	-2(1)	0(1)	1(1)
C5	36(1)	38(1)	33(1)	-4(1)	1(1)	2(1)
C6	34(1)	37(1)	24(1)	-2(1)	2(1)	2(1)
C7	30(1)	30(1)	32(1)	3(1)	3(1)	0(1)
C8	27(1)	32(1)	29(1)	2(1)	-2(1)	-4(1)
C9	37(1)	30(1)	31(1)	7(1)	-3(1)	5(1)
C10	40(1)	34(1)	33(1)	0(1)	1(1)	1(1)
C11	39(1)	30(1)	31(1)	4(1)	-5(1)	3(1)
C12	42(1)	31(1)	36(1)	-1(1)	-1(1)	1(1)
C13	43(1)	35(1)	33(1)	1(1)	3(1)	6(1)
C14	38(1)	32(1)	30(1)	3(1)	-3(1)	-1(1)
C15	46(1)	36(1)	37(1)	-3(1)	3(1)	1(1)
C16	46(1)	35(1)	41(1)	-6(1)	1(1)	-5(1)
C17	40(1)	36(1)	30(1)	1(1)	-3(1)	-1(1)
C18	43(1)	34(1)	28(1)	1(1)	0(1)	0(1)
C19	39(1)	31(1)	28(1)	0(1)	0(1)	-2(1)
C20	38(1)	35(1)	35(1)	1(1)	-4(1)	-2(1)
C21	48(1)	53(1)	34(1)	-5(1)	-5(1)	-5(1)
C22	45(1)	57(1)	46(1)	-8(1)	-16(1)	-7(1)
C23	34(1)	48(1)	49(1)	-5(1)	-8(1)	-2(1)
C24	36(1)	39(1)	41(1)	-2(1)	-2(1)	0(1)
C25	36(1)	29(1)	34(1)	0(1)	-6(1)	0(1)
C26	30(1)	31(1)	28(1)	1(1)	2(1)	-4(1)
C27	33(1)	28(1)	31(1)	-1(1)	1(1)	-1(1)
C28	32(1)	30(1)	37(1)	1(1)	-3(1)	-1(1)
C29	37(1)	33(1)	38(1)	-1(1)	-5(1)	1(1)
C30	31(1)	37(1)	49(1)	-4(1)	-7(1)	-1(1)

C31	33(1)	40(1)	48(1)	-2(1)	2(1)	-1(1)
C32	36(1)	38(1)	38(1)	3(1)	-2(1)	-4(1)
C33	32(1)	30(1)	36(1)	4(1)	-3(1)	-1(1)
C34	30(1)	34(1)	31(1)	-1(1)	0(1)	2(1)
C35	32(1)	30(1)	32(1)	1(1)	2(1)	-2(1)
C36	33(1)	31(1)	34(1)	-2(1)	-5(1)	-3(1)
C37	38(1)	32(1)	31(1)	-1(1)	-4(1)	1(1)
C38	36(1)	31(1)	31(1)	-2(1)	-6(1)	-5(1)
C39	38(1)	42(1)	31(1)	4(1)	-4(1)	-3(1)
C40	34(1)	38(1)	38(1)	1(1)	-8(1)	-1(1)
C41	39(1)	32(1)	34(1)	-1(1)	-1(1)	-4(1)
C42	41(1)	45(1)	34(1)	1(1)	-1(1)	-2(1)
C43	50(1)	43(1)	32(1)	-1(1)	3(1)	-6(1)
C44	42(1)	33(1)	37(1)	-2(1)	4(1)	-4(1)
C45	42(1)	35(1)	34(1)	0(1)	2(1)	-2(1)
C46	40(1)	32(1)	31(1)	0(1)	4(1)	-1(1)
C47	46(1)	40(1)	37(1)	-4(1)	6(1)	-7(1)
C48	53(1)	42(1)	53(1)	2(1)	9(1)	-6(1)
C49	64(2)	49(1)	72(2)	10(1)	23(1)	-12(1)
C50	50(1)	58(2)	77(2)	7(1)	23(1)	-5(1)
C51	47(1)	52(1)	58(1)	5(1)	14(1)	0(1)
C52	43(1)	44(1)	37(1)	-2(1)	5(1)	-4(1)
C53	39(1)	38(1)	36(1)	-4(1)	8(1)	3(1)
C54	32(1)	41(1)	40(1)	-3(1)	4(1)	2(1)
N1	41(1)	35(1)	37(1)	2(1)	1(1)	-1(1)
N2	38(1)	39(1)	34(1)	-2(1)	-1(1)	1(1)

Table 8.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8.8**.

	x	y	z	U(eq)
H2	-975	7404	9569	47
H3	-1864	7012	9522	51
H4	-1966	6041	9473	49
H5	-1183	5470	9533	43
H8	-307	5216	8942	36
H10	307	6440	8884	43
H12	774	8022	9877	44
H13	-72	7580	10064	44
H15	1466	8524	9460	48
H16	2328	8890	9197	48
H18	2682	7448	8395	42
H19	1842	7077	8682	39
H21	3300	8787	9376	54
H47A	4208	9093	9213	59
H23	4641	8908	8369	52
H24	4154	8433	7667	46
H27	2506	8660	7572	37
H29	1125	6834	10495	43
H30	298	6828	10996	47
H31	314	6903	11971	48
H23A	1162	7046	12428	45
H35	2131	6572	12632	38
H37	2620	6469	11383	40
H39	2725	7180	9598	44
H40	1916	7330	10122	44
H42	3432	6828	9094	48
H43	4281	6629	8667	50
H45	4912	6146	10154	45
H46	4074	6358	10580	41

H48	5263	6987	8662	59
H49	6168	6912	8326	74
H50	6728	6162	8593	74
H51	6359	5463	9154	63
H54	5955	5304	10165	45

Table 8.6. Torsion angles [°] for **8.8**.

C6-C1-C2-C3	-3.1(3)	C11-C14-C15-C16	179.90(18)
C9-C1-C2-C3	170.30(19)	C14-C15-C16-C17	1.2(3)
C1-C2-C3-C4	0.4(3)	C15-C16-C17-C18	-0.9(3)
C2-C3-C4-C5	2.4(3)	C15-C16-C17-C20	-176.12(19)
C3-C4-C5-C6	-2.5(3)	C16-C17-C18-C19	-0.3(3)
C4-C5-C6-C1	-0.2(3)	C20-C17-C18-C19	175.03(17)
C4-C5-C6-C7	177.03(18)	C17-C18-C19-C14	1.1(3)
C2-C1-C6-C5	2.9(3)	C15-C14-C19-C18	-0.9(3)
C9-C1-C6-C5	-170.11(17)	C11-C14-C19-C18	178.98(17)
C2-C1-C6-C7	-174.19(17)	C16-C17-C20-C21	40.5(3)
C9-C1-C6-C7	12.8(3)	C18-C17-C20-C21	-134.6(2)
C5-C6-C7-C8#1	-124.74(19)	C16-C17-C20-C25	-143.2(2)
C1-C6-C7-C8#1	52.4(3)	C18-C17-C20-C25	41.7(3)
C5-C6-C7-C8	53.1(2)	C25-C20-C21-C22	-0.8(3)
C1-C6-C7-C8	-129.70(19)	C17-C20-C21-C22	175.7(2)
C8#1-C7-C8-C7#4	0.0(3)	C20-C21-C22-C23	-0.7(4)
C6-C7-C8-C7#4	-177.91(12)	C21-C22-C23-C24	1.0(4)
C2-C1-C9-C10	-128.1(2)	C22-C23-C24-C25	0.2(3)
C6-C1-C9-C10	45.0(3)	C23-C24-C25-C20	-1.7(3)
C2-C1-C9-C13	45.5(3)	C23-C24-C25-C26	174.43(19)
C6-C1-C9-C13	-141.44(19)	C21-C20-C25-C24	1.9(3)
C13-C9-C10-N1	-0.6(3)	C17-C20-C25-C24	-174.38(18)
C1-C9-C10-N1	173.49(17)	C21-C20-C25-C26	-173.98(18)
N1-C11-C12-C13	-1.7(3)	C17-C20-C25-C26	9.7(3)
C14-C11-C12-C13	179.07(18)	C24-C25-C26-C27#1	58.8(2)
C11-C12-C13-C9	1.4(3)	C20-C25-C26-C27#1	-125.2(2)
C10-C9-C13-C12	-0.3(3)	C24-C25-C26-C27	-117.2(2)
C1-C9-C13-C12	-174.15(17)	C20-C25-C26-C27	58.8(2)
N1-C11-C14-C19	-15.2(2)	C27#1-C26-C27-C26#4	-0.1(3)
C12-C11-C14-C19	164.02(18)	C25-C26-C27-C26#4	175.95(12)
N1-C11-C14-C15	164.63(18)	C33-C28-C29-C30	-1.6(3)
C12-C11-C14-C15	-16.1(3)	C36-C28-C29-C30	175.00(18)
C19-C14-C15-C16	-0.3(3)	C28-C29-C30-C31	-1.4(3)

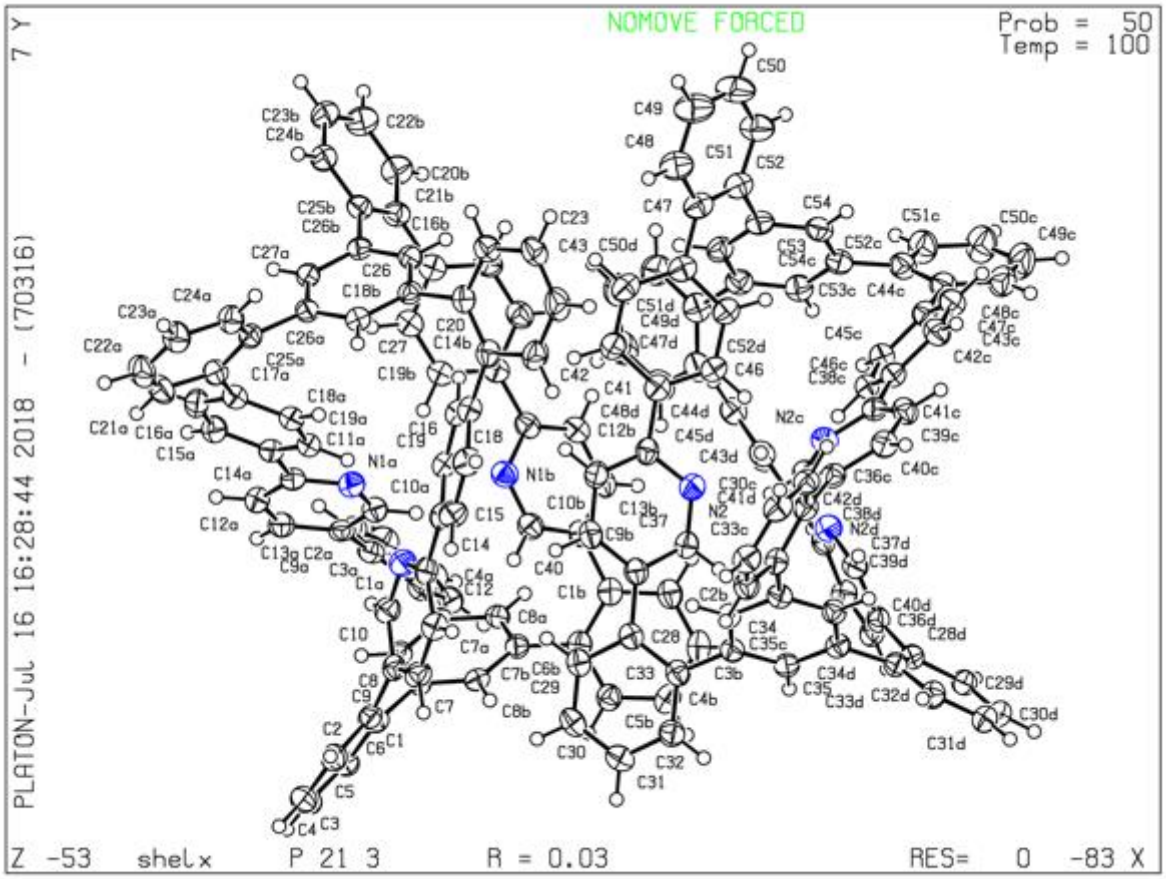
C29-C30-C31-C32	2.5(3)	C42-C43-C44-C47	-175.47(19)
C30-C31-C32-C33	-0.5(3)	C43-C44-C45-C46	0.3(3)
C31-C32-C33-C28	-2.5(3)	C47-C44-C45-C46	175.06(18)
C31-C32-C33-C34	173.07(18)	C44-C45-C46-C41	0.9(3)
C29-C28-C33-C32	3.5(3)	C42-C41-C46-C45	-1.5(3)
C36-C28-C33-C32	-172.99(17)	C38-C41-C46-C45	179.49(17)
C29-C28-C33-C34	-171.85(17)	C45-C44-C47-C48	-129.8(2)
C36-C28-C33-C34	11.7(3)	C43-C44-C47-C48	44.7(3)
C32-C33-C34-C35	55.6(2)	C45-C44-C47-C52	45.0(3)
C28-C33-C34-C35	-129.0(2)	C43-C44-C47-C52	-140.5(2)
C32-C33-C34-C35#2	-121.0(2)	C52-C47-C48-C49	-1.5(4)
C28-C33-C34-C35#2	54.3(3)	C44-C47-C48-C49	173.5(2)
C35#2-C34-C35-C34#3	-0.6(4)	C47-C48-C49-C50	-1.1(4)
C33-C34-C35-C34#3	-177.29(12)	C48-C49-C50-C51	2.1(4)
C29-C28-C36-C40	38.8(3)	C49-C50-C51-C52	-0.5(4)
C33-C28-C36-C40	-144.76(19)	C50-C51-C52-C47	-2.2(4)
C29-C28-C36-C37	-135.73(19)	C50-C51-C52-C53	174.4(2)
C33-C28-C36-C37	40.7(3)	C48-C47-C52-C51	3.1(3)
C40-C36-C37-N2	-0.8(3)	C44-C47-C52-C51	-171.7(2)
C28-C36-C37-N2	174.07(17)	C48-C47-C52-C53	-173.3(2)
N2-C38-C39-C40	-1.3(3)	C44-C47-C52-C53	11.9(3)
C41-C38-C39-C40	179.99(17)	C51-C52-C53-C54	55.5(3)
C37-C36-C40-C39	0.2(3)	C47-C52-C53-C54	-128.1(2)
C28-C36-C40-C39	-174.55(18)	C51-C52-C53-C54#3	-121.5(2)
C38-C39-C40-C36	0.8(3)	C47-C52-C53-C54#3	54.9(3)
N2-C38-C41-C46	-13.5(2)	C54#3-C53-C54-C53#2	0.1(4)
C39-C38-C41-C46	165.29(19)	C52-C53-C54-C53#2	-176.86(13)
N2-C38-C41-C42	167.61(18)	C9-C10-N1-C11	0.2(3)
C39-C38-C41-C42	-13.6(3)	C12-C11-N1-C10	0.9(3)
C46-C41-C42-C43	1.0(3)	C14-C11-N1-C10	-179.82(16)
C38-C41-C42-C43	179.87(18)	C36-C37-N2-C38	0.3(3)
C41-C42-C43-C44	0.3(3)	C39-C38-N2-C37	0.7(3)
C42-C43-C44-C45	-0.9(3)	C41-C38-N2-C37	179.56(16)

Symmetry transformations used to generate equivalent atoms:

#1 y-1/2,-z+3/2,-x+1 #2 -z+3/2,-x+1,y+1/2 #3 -y+1,z-1/2,-x+3/2

#4 -z+1,x+1/2,-y+3/2

Figure 8.6. View of **8.8** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



X-ray Experimental for $(C_{81}H_{48}N_3)Ir\text{-}H_2O$: Crystals grew as orange prisms by vapor diffusion of pentane to DCM. The data crystal was broken from a larger crystal and had approximate dimensions; 0.12 x 0.074 x 0.042 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 251 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 35 seconds per frame using a detector offset of -42.7° and a counting time of 135 seconds per frame using a detector offset of 110.4°. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46.[1] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON[4] and WinGX.[5] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom. A single atom was encapsulated in the cryptand. It was assumed to be a water molecule. The cryptand resides on a crystallographic three-fold rotation axis.

A large solvent void was found in the unit cell containing only very diffuse electron density. The contributions to the scattering factors due to this solvent region were removed by use of the utility SQUEEZE[6] in PLATON. PLATON was used as incorporated in WinGX.

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0928*P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_w(F^2)$ refined to 0.163, with R(F) equal to 0.0555 and a goodness of fit, S, = 1.01. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given

below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

Table 8.7. Crystal data and structure refinement for **8.9**.

Empirical formula	C81 H48 Ir N3 O	
Formula weight	1271.42	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	cubic	
Space group	P 43 3 2	
Unit cell dimensions	a = 24.2181(8) Å	α= 90°.
	b = 24.2181(8) Å	β= 90°.
	c = 24.2181(8) Å	γ = 90°.
Volume	14204.3(14) $Å^3$	
Z	8	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	3.973 mm^{-1}	
F(000)	5120	
Crystal size	0.120 x 0.074 x 0.042 mm^3	
Theta range for data collection	2.580 to 68.219°.	
Index ranges	-27<=h<=21, -21<=k<=29, -24<=l<=16	
Reflections collected	20809	
Independent reflections	4354 [R(int) = 0.0809]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.466	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4354 / 0 / 260	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1413	
R indices (all data)	R1 = 0.0849, wR2 = 0.1631	
Absolute structure parameter	0.02(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.034 and -0.413 $e.Å^{-3}$	

Table 8.8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8.9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	5134(6)	678(5)	5108(5)	79(3)
C2	5571(5)	357(5)	5211(5)	78(3)
C3	5942(7)	461(5)	5702(6)	94(5)
C4	6515(6)	540(5)	5654(6)	85(4)
C5	6817(9)	586(7)	6128(7)	119(7)
C6	6593(10)	567(6)	6638(9)	131(8)
C7	6024(11)	510(7)	6698(7)	126(7)
C8	5697(8)	441(6)	6211(6)	100(5)
C9	6793(6)	607(5)	5098(6)	88(5)
C10	6573(5)	919(4)	4688(5)	72(3)
C11	7336(5)	804(5)	4104(7)	88(4)
C12	7586(5)	511(5)	4524(7)	95(5)
C13	7327(6)	419(5)	5014(7)	92(5)
C14	7552(5)	917(5)	3547(7)	84(4)
C15	7224(4)	1216(5)	3185(6)	73(3)
C16	7407(5)	1323(5)	2667(6)	81(4)
C17	7944(5)	1149(5)	2502(7)	87(4)
C18	8243(6)	849(6)	2879(9)	108(6)
C19	8066(6)	730(6)	3395(8)	95(4)
C20	8141(6)	1267(6)	1912(8)	99(5)
C21	8082(6)	1763(7)	1660(7)	101(5)
C22	8227(8)	1837(8)	1086(8)	120(6)
C23	8451(10)	1400(9)	801(9)	147(8)
C24	8499(11)	888(8)	1048(12)	161(11)
C25	8340(8)	827(8)	1609(10)	131(7)
C26	7902(5)	2279(5)	1963(5)	78(3)
C27	8198(5)	2452(5)	2429(6)	82(3)
Ir1	6477(1)	1477(1)	3523(1)	70(1)
N1	6809(4)	1014(4)	4215(4)	70(2)
O1W	5718(3)	718(3)	4282(3)	54(3)

Table 8.9. Bond lengths [Å] and angles [°] for **8.8**.

C1-C2	1.336(17)	C15-C16	1.356(18)
C1-C2#1	1.427(16)	C15-Ir1	2.084(10)
C1-H1	0.95	C16-C17	1.422(17)
C2-C3	1.512(17)	C16-H16	0.95
C3-C8	1.37(2)	C17-C18	1.37(2)
C3-C4	1.41(2)	C17-C20	1.54(2)
C4-C5	1.366(19)	C18-C19	1.35(2)
C4-C9	1.51(2)	C18-H18	0.95
C5-C6	1.35(3)	C19-H19	0.95
C5-H5	0.95	C20-C21	1.35(2)
C6-C7	1.39(3)	C20-C25	1.38(2)
C6-H6	0.95	C21-C22	1.45(3)
C7-C8	1.43(2)	C21-C26	1.513(18)
C7-H7	0.95	C22-C23	1.38(2)
C8-H8	0.95	C22-H22	0.95
C9-C10	1.358(17)	C23-C24	1.38(3)
C9-C13	1.39(2)	C23-H23	0.95
C10-N1	1.301(16)	C24-C25	1.42(3)
C10-H10	0.95	C24-H24	0.95
C11-C12	1.379(18)	C25-H25	0.95
C11-N1	1.399(17)	C26-C27#2	1.358(18)
C11-C14	1.47(2)	C26-C27	1.400(18)
C12-C13	1.36(2)	C27-H27	0.95
C12-H12	0.95	Ir1-N1#2	2.170(9)
C13-H13	0.95	Ir1-N1#1	2.170(9)
C14-C19	1.37(2)	Ir1-N1	2.170(9)
C14-C15	1.388(19)		

C2-C1-C2#1	120.3(12)	C1#2-C2-C3	118.9(11)
C2-C1-H1	119.8	C8-C3-C4	120.5(13)
C2#1-C1-H1	119.8	C8-C3-C2	116.3(15)
C1-C2-C1#2	119.6(12)	C4-C3-C2	123.1(13)
C1-C2-C3	121.4(12)	C5-C4-C3	118.1(16)

C5-C4-C9	120.0(15)	C15-C16-C17	120.2(13)
C3-C4-C9	121.8(11)	C15-C16-H16	119.9
C6-C5-C4	123.4(19)	C17-C16-H16	119.9
C6-C5-H5	118.3	C18-C17-C16	116.9(15)
C4-C5-H5	118.3	C18-C17-C20	123.6(13)
C5-C6-C7	119.9(16)	C16-C17-C20	119.3(14)
C5-C6-H6	120.1	C19-C18-C17	123.9(14)
C7-C6-H6	120.1	C19-C18-H18	118.0
C6-C7-C8	118.3(19)	C17-C18-H18	118.0
C6-C7-H7	120.9	C18-C19-C14	117.8(15)
C8-C7-H7	120.9	C18-C19-H19	121.1
C3-C8-C7	119.8(19)	C14-C19-H19	121.1
C3-C8-H8	120.1	C21-C20-C25	118.8(19)
C7-C8-H8	120.1	C21-C20-C17	123.5(13)
C10-C9-C13	116.2(15)	C25-C20-C17	117.4(16)
C10-C9-C4	122.4(14)	C20-C21-C22	121.2(14)
C13-C9-C4	120.8(12)	C20-C21-C26	123.0(15)
N1-C10-C9	124.8(13)	C22-C21-C26	115.7(16)
N1-C10-H10	117.6	C23-C22-C21	119(2)
C9-C10-H10	117.6	C23-C22-H22	120.6
C12-C11-N1	116.5(15)	C21-C22-H22	120.6
C12-C11-C14	128.0(14)	C22-C23-C24	120(2)
N1-C11-C14	115.5(11)	C22-C23-H23	119.8
C13-C12-C11	121.7(14)	C24-C23-H23	119.8
C13-C12-H12	119.1	C23-C24-C25	119.0(17)
C11-C12-H12	119.1	C23-C24-H24	120.5
C12-C13-C9	120.3(13)	C25-C24-H24	120.5
C12-C13-H13	119.9	C20-C25-C24	122(2)
C9-C13-H13	119.9	C20-C25-H25	119.2
C19-C14-C15	121.4(15)	C24-C25-H25	119.2
C19-C14-C11	120.4(14)	C27#2-C26-C27	119.2(13)
C15-C14-C11	118.2(12)	C27#2-C26-C21	121.5(13)
C16-C15-C14	119.7(12)	C27-C26-C21	119.3(12)
C16-C15-Ir1	126.3(10)	C26#1-C27-C26	120.8(13)
C14-C15-Ir1	114.0(10)	C26#1-C27-H27	119.6

C26-C27-H27	119.6	N1#2-Ir1-N1#1	94.6(4)
C15#1-Ir1-C15#2	92.3(5)	C15#1-Ir1-N1	93.9(4)
C15#1-Ir1-C15	92.3(5)	C15#2-Ir1-N1	170.2(4)
C15#2-Ir1-C15	92.3(5)	C15-Ir1-N1	79.9(5)
C15#1-Ir1-N1#2	170.2(4)	N1#2-Ir1-N1	94.6(4)
C15#2-Ir1-N1#2	79.9(5)	N1#1-Ir1-N1	94.6(4)
C15-Ir1-N1#2	93.9(4)	C10-N1-C11	120.3(11)
C15#1-Ir1-N1#1	79.9(5)	C10-N1-Ir1	127.4(8)
C15#2-Ir1-N1#1	93.9(4)	C11-N1-Ir1	112.3(9)
C15-Ir1-N1#1	170.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -z+1,x-1/2,-y+1/2 #2 y+1/2,-z+1/2,-x+1

Table 8.10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8.9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	105(10)	72(7)	60(7)	-11(6)	-4(6)	14(7)
C2	86(8)	77(8)	72(7)	3(6)	-21(6)	11(6)
C3	135(14)	69(7)	79(9)	-4(6)	-35(9)	7(8)
C4	98(9)	61(7)	97(9)	5(6)	-33(8)	-1(7)
C5	160(16)	82(10)	116(13)	36(10)	-69(13)	-37(10)
C6	170(20)	75(9)	144(17)	20(10)	-85(15)	-38(11)
C7	200(20)	82(10)	94(11)	-7(8)	-50(14)	9(13)
C8	135(13)	77(9)	88(10)	-2(7)	-35(9)	7(9)
C9	102(10)	49(6)	114(11)	16(7)	-50(9)	-17(6)
C10	83(8)	47(5)	86(8)	-14(5)	-19(7)	-8(5)
C11	74(7)	47(6)	142(13)	2(7)	-37(8)	-11(5)
C12	73(8)	57(7)	156(14)	31(8)	-46(9)	0(6)
C13	88(10)	64(7)	124(12)	25(7)	-48(9)	-13(7)
C14	76(8)	54(7)	123(11)	-16(7)	-13(8)	-8(6)
C15	40(5)	87(8)	91(9)	-19(6)	8(5)	5(5)
C16	65(7)	58(6)	121(11)	-13(7)	-8(7)	7(5)
C17	73(8)	53(7)	135(12)	-13(7)	16(8)	-2(6)
C18	62(8)	63(8)	200(20)	1(10)	16(10)	5(6)
C19	85(9)	64(8)	135(14)	9(8)	-10(9)	-12(7)
C20	83(10)	66(7)	148(15)	-25(9)	20(9)	-13(7)
C21	78(8)	104(12)	121(12)	-30(9)	8(8)	9(8)
C22	117(13)	116(13)	128(14)	-32(13)	-2(12)	25(10)
C23	180(20)	133(17)	130(14)	-42(14)	46(15)	26(16)
C24	190(20)	88(12)	210(30)	-45(15)	70(20)	-4(13)
C25	122(14)	96(11)	170(20)	-29(12)	39(13)	1(10)
C26	81(8)	73(7)	80(8)	-10(6)	9(6)	4(6)
C27	87(8)	64(8)	94(10)	2(6)	-11(7)	4(6)
Ir1	70(1)	70(1)	70(1)	-12(1)	-12(1)	12(1)
N1	77(6)	58(5)	73(5)	10(5)	-17(5)	1(5)
O1W	54(3)	54(3)	54(3)	-13(3)	-13(3)	13(3)

Table 8.11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8.9**.

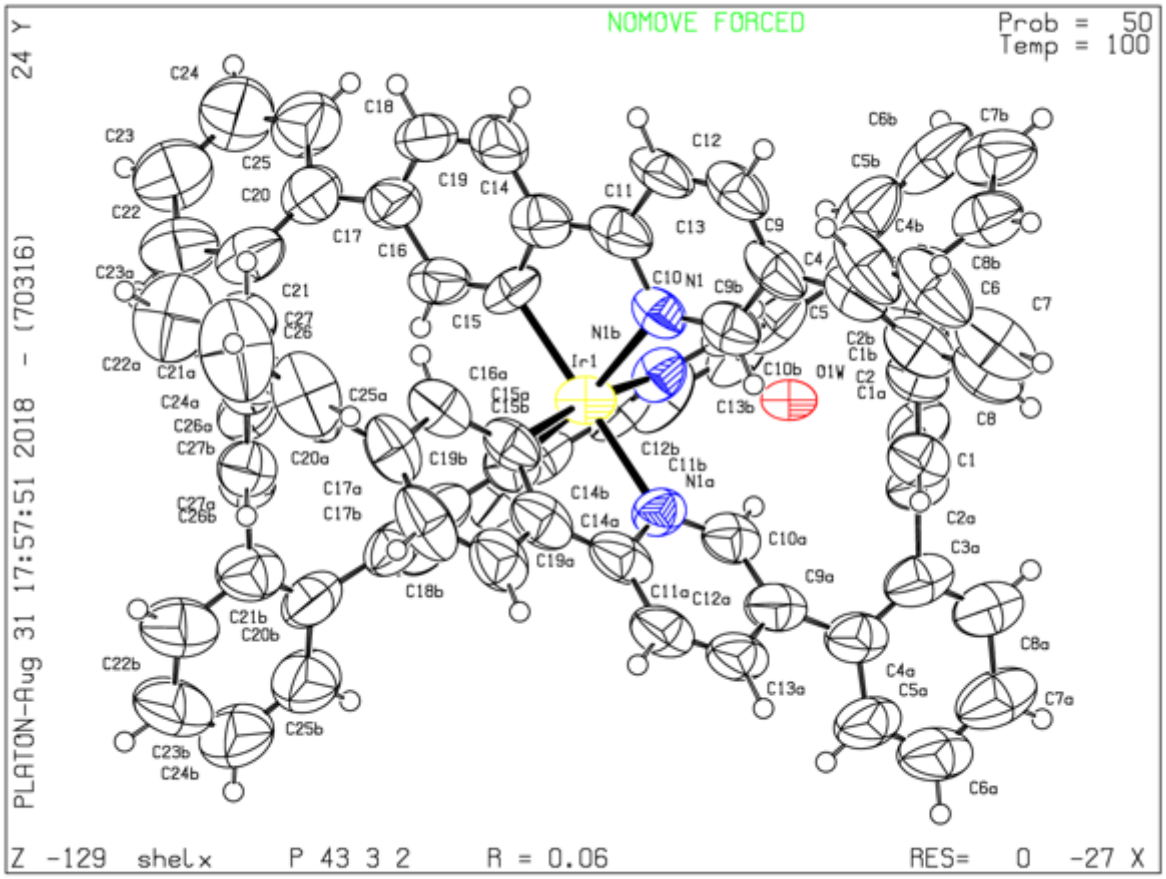
	x	y	z	U(eq)
H1	5053	980	5346	94
H5	7205	634	6098	143
H6	6822	593	6955	157
H7	5858	518	7053	151
H8	5311	380	6241	120
H10	6221	1079	4751	86
H12	7947	369	4469	114
H13	7514	226	5300	110
H16	7177	1514	2413	98
H18	8597	717	2771	129
H19	8288	524	3643	114
H22	8169	2182	909	144
H23	8573	1450	432	177
H24	8637	581	846	194
H25	8371	476	1779	157
H27	8516	2252	2542	98

Table 8.12. Torsion angles [°] for **8.9**.

C2#1-C1-C2-C1#2	-2(3)	C11-C14-C15-C16	-179.3(11)
C2#1-C1-C2-C3	-179.8(10)	C19-C14-C15-Ir1	-177.9(10)
C1-C2-C3-C8	59.8(19)	C11-C14-C15-Ir1	2.0(14)
C1#2-C2-C3-C8	-117.6(16)	C14-C15-C16-C17	-2.7(18)
C1-C2-C3-C4	-124.2(16)	Ir1-C15-C16-C17	175.8(9)
C1#2-C2-C3-C4	58.4(19)	C15-C16-C17-C18	3.5(19)
C8-C3-C4-C5	1(2)	C15-C16-C17-C20	179.2(11)
C2-C3-C4-C5	-174.8(13)	C16-C17-C18-C19	-2(2)
C8-C3-C4-C9	-175.5(12)	C20-C17-C18-C19	-178.0(14)
C2-C3-C4-C9	9(2)	C17-C18-C19-C14	1(2)
C3-C4-C5-C6	-1(2)	C15-C14-C19-C18	0(2)
C9-C4-C5-C6	175.6(15)	C11-C14-C19-C18	-179.6(12)
C4-C5-C6-C7	-1(3)	C18-C17-C20-C21	-138.3(17)
C5-C6-C7-C8	4(3)	C16-C17-C20-C21	46(2)
C4-C3-C8-C7	1(2)	C18-C17-C20-C25	48(2)
C2-C3-C8-C7	177.3(13)	C16-C17-C20-C25	-127.4(17)
C6-C7-C8-C3	-4(2)	C25-C20-C21-C22	0(3)
C5-C4-C9-C10	-134.5(14)	C17-C20-C21-C22	-174.0(16)
C3-C4-C9-C10	42.0(18)	C25-C20-C21-C26	-176.1(16)
C5-C4-C9-C13	35.5(19)	C17-C20-C21-C26	10(2)
C3-C4-C9-C13	-148.0(13)	C20-C21-C22-C23	-3(3)
C13-C9-C10-N1	5.6(17)	C26-C21-C22-C23	173.1(18)
C4-C9-C10-N1	176.0(10)	C21-C22-C23-C24	5(4)
N1-C11-C12-C13	1.5(19)	C22-C23-C24-C25	-3(4)
C14-C11-C12-C13	-177.3(12)	C21-C20-C25-C24	2(3)
C11-C12-C13-C9	2(2)	C17-C20-C25-C24	176(2)
C10-C9-C13-C12	-5.4(18)	C23-C24-C25-C20	0(4)
C4-C9-C13-C12	-176.0(12)	C20-C21-C26-C27#2	-123.3(17)
C12-C11-C14-C19	-1.1(19)	C22-C21-C26-C27#2	61(2)
N1-C11-C14-C19	-179.9(11)	C20-C21-C26-C27	55(2)
C12-C11-C14-C15	178.9(12)	C22-C21-C26-C27	-120.7(16)
N1-C11-C14-C15	0.1(15)	C27#2-C26-C27-C26#1	1(3)
C19-C14-C15-C16	0.7(19)	C21-C26-C27-C26#1	-177.8(11)

C9-C10-N1-C11	-2.1(17)	C14-C11-N1-C10	177.4(9)
C9-C10-N1-Ir1	177.2(8)	C12-C11-N1-Ir1	179.0(9)
C12-C11-N1-C10	-1.6(16)	C14-C11-N1-Ir1	-2.0(12)

Figure 8.7. View of **8.9** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



Appendix

acac	Acetylacetonate
$AdCO_2H$	1-Adamantane carboxylic acid
Ar	Aaryl
BINAP	2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl
BIPHEP	2,2'-Bis(diphenylphosphino)-1,1'-biphenyl
*t*Bu	*tert*-Butyl
t-BuOK	Potassium *tert*-butoxide
CD	Circular Dichroism
cod	Cycloocta-1,5-diene
cot	Cycloocta-1,3,5,7-tetraene
CHD	1,3-Cyclohexadiene
Cy	Cyclohexane
CyJohnPhos	(2-Biphenyl)dicyclohexylphosphine
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DMac	N,N-Dimethylacetamide
DM-SEGPHOS	5,5′-Bis[di(3,5-xylyl)phosphino]-4,4′-bi-1,3-benzodioxole
DMF	N,N-Dimethyl fromamide
2-DPPBN	2-(Diphenylphosphino)benzonitrile
dCype	1,2-Bis(dicyclohexylphosphino)ethane
DMSO	Dimethyl sulfoxide
dppe	1,2-Bis(diphenylphosphino)ethane

dppp	1,3-Bis(diphenylphosphino)propane
eq	Equivalent
ESI	Electrospray ionization
EtOAc	Ethylacetate
FTIR	Fourier Transform Infrared
HBC	Hexa-*peri*-hexabenzocoronenes
Hex	Hexyl
LCMS	Liquid chromatography–mass spectrometry
LDA	Lithium diisopropylamide
MALDI	Matrix-assisted laser desorption/ionization
MeCN	Acetonitrile
MeOH	Methanol
3,5-Me_2BzOH	3,5-Dimethyl Benzoic acid
MP	Melting point
MS	Mass spectrometry
NBD	Norbornadiene
NEt_3	Triethylamine
NHC	N-heterocyclic carbene
NMO	N-methylmorpholine N-oxide
NMR	Nuclear magnetic resonance spectroscopy
O-Ac	Acetate
O-Piv	Trimethylacetate
O-TPA	Triphenyl acetates

OLED	Organic light-emitting diode
PAH	Polycyclic aromatic hydrocarbon
PBu_3	Tri(*n*-butyl)phosphine
PCTD	Pentacyclo[5.4.2$^{1.7}$.1$^{3.6}$.0$^{10.13}$.0$^{12.14}$]tetradeca-4,8-diene
PCy_3	Tricyclohexylphosphine
$Pd(PPh_3)Cl_2$	Palladium tetrakis(triphenylphosphine)
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
PEt_3	Triethylphosphine
PhMe	Toluene
PMP	*para*-methoxyphenyl
PPh_3	Triphenyl phosphine
ppy	Phenyl pyridine
c-Pr	Cyclopropyl
*i*Pr	*iso*-Propyl
PTSA•H_2O	*para*-Toluenesulfonic acid monohydrate
RuPhos	2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl
Tf	Trifluoromethane
TLC	Thin-layer chromatography
TMS	Trimethylsily
TES	Triethylsilane
THF	Tetrahydrofuran
TOF	Time-of-flight
p-TsOH	*para*-Toluenesulfonic acid

Ts	*p*-Toluenesulfonyl
XPhos	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl

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(24) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.

$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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